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NEWS 23	AUG 15	CAOLD to be discontinued on December 31, 2008
NEWS 24	AUG 15	CAplus currency for Korean patents enhanced
NEWS 25	AUG 25	CA/CAplus, CASREACT, and IFI and USPAT databases enhanced for more flexible patent number searching
NEWS 26	AUG 27	CAS definition of basic patents expanded to ensure comprehensive access to substance and sequence information

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FILE LAST UPDATED: 16 Sep 2008 (20080916/ED)

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=> s (?esterification) (L) ((methyl (a) acetate) or (ethyl (a) acetate) or formate or propionate)
126891 ?ESTERIFICATION
1069165 METHYL

```
          717 METHYLS
      1069597 METHYL
                (METHYL OR METHYLS)
       979707 ME
        11297 MES
       986913 ME
                (ME OR MES)
      1699369 METHYL
                (METHYL OR ME)
       573680 ACETATE
        30105 ACETATES
       586084 ACETATE
                (ACETATE OR ACETATES)
       505356 ETHYL
           43 ETHYLS
       505382 ETHYL
                (ETHYL OR ETHYLS)
       690323 ET
         8598 ETS
       697316 ET
                (ET OR ETS)
      1054585 ETHYL
                (ETHYL OR ET)
       573680 ACETATE
        30105 ACETATES
       586084 ACETATE
                (ACETATE OR ACETATES)
        44864 FORMATE
         3678 FORMATES
        46235 FORMATE
                (FORMATE OR FORMATES)
        50853 PROPIONATE
         2073 PROPIONATES
        51923 PROPIONATE
                (PROPIONATE OR PROPIONATES)
L1         2441 (?ESTERIFICATION) (L) ((METHYL (A) ACETATE) OR (ETHYL (A) ACETAT
                E) OR FORMATE OR PROPIONATE)

=> s l1 (L) (fat# or oil#)
       324865 FAT#
       970002 OIL#
L2          177 L1 (L) (FAT# OR OIL#)

=> s l2 and (lipase or enzyme)
        53203 LIPASE
         9156 LIPASES
        54630 LIPASE
                (LIPASE OR LIPASES)
       866752 ENZYME
       495514 ENZYMES
      1095254 ENZYME
                (ENZYME OR ENZYMES)
L3           27 L2 AND (LIPASE OR ENZYME)

=> s l3 and fuel
       446610 FUEL
       177049 FUELS
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```
        501158 FUEL
                  (FUEL OR FUELS)
L4           14 L3 AND FUEL

=> d l4 1-7 ibib abs

L4   ANSWER 1 OF 14  CAPLUS  COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER:         2008:562374  CAPLUS
TITLE:                    Lipase-catalyzed biodiesel production with
                          methyl acetate as acyl acceptor
AUTHOR(S):                Huang, Ying; Yan, Yunjun
CORPORATE SOURCE:         School of Life Science & Technology, Huazhong
                          University of Science and Technology, Wuhan, 430074,
                          Peop. Rep. China
SOURCE:                   Zeitschrift fuer Naturforschung, C: Journal of
                          Biosciences (2008), 63(3/4), 297-302
                          CODEN: ZNCBDA; ISSN: 0939-5075
PUBLISHER:                Verlag der Zeitschrift fuer Naturforschung
DOCUMENT TYPE:            Journal
LANGUAGE:                 English
AB   Biodiesel is an alternative diesel fuel made from renewable
     biol. resources.  During the process of biodiesel production, lipase
     -catalyzed transesterification is a crucial step.  However,
     current techniques using methanol as acyl acceptor have lower enzymic
     activity; this limits the application of such techniques in large-scale
     biodiesel production  Furthermore, the lipid feedstock of currently available
     techniques is limited.  In this paper, the technique of lipase
     -catalyzed transesterification of five different oils
     for biodiesel production with Me acetate as acyl acceptor
     was investigated, and the transesterification reaction
     conditions were optimized.  The operation stability of lipase
     under the obtained optimal conditions was further examined  The results
     showed that under optimal transesterification conditions, both
     plant oils and animal fats led to high yields of Me
     ester: cotton-seed oil, 98%; rape-seed oil, 95%;
     soybean oil, 91%; tea-seed oil, 92%; and lard, 95%.
     Crude and refined cotton-seed oil or lard made no significant
     difference in yields of Me ester.  No loss of enzymic activity was
     detected for lipase after being repeatedly used for 40 cycles
     (ca. 800 h), which indicates that the operational stability of
     lipase was fairly good under these conditions.  Our results
     suggest that cotton-seed oil, rape-seed oil and lard
     might substitute soybean oil as suitable lipid feedstock for
     biodiesel production  Our results also show that our technique is fit for
     various lipid feedstocks both from plants and animals, and presents a very
     promising way for the large-scale biodiesel production
REFERENCE COUNT:          21    THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS
                                RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4   ANSWER 2 OF 14  CAPLUS  COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER:         2008:128012  CAPLUS
DOCUMENT NUMBER:          148:264711
TITLE:                    Environmental friendly method for production of
                          biodiesel
INVENTOR(S):              Weng, Tianbo
PATENT ASSIGNEE(S):       Shanghai CNPC Enterprise Group Co., Ltd., Peop. Rep.
                          China
```

SOURCE: Faming Zhuanli Shenqing Gongkai Shuomingshu, 5pp.
CODEN: CNXXEV
DOCUMENT TYPE: Patent
LANGUAGE: Chinese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
CN 101113354	A	20080130	CN 2006-10029460	20060727

PRIORITY APPLN. INFO.: CN 2006-10029460 20060727

AB The title method comprises the steps of: mixing short-chain fatty acid ester (Me acetate or Et acetate) as the acyl receptor with animal and vegetable oils at a mol. ratio of (3-15):1, and performing transesterification reaction by lipase catalysis for 4-15 h to obtain biodiesel. The method has the advantages of mild reaction conditions, simple process and easy control, and is environmental friendly.

L4 ANSWER 3 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2007:1342659 CAPLUS
DOCUMENT NUMBER: 149:227633
TITLE: Study on rapeseed oil extraction by methyl acetate coupling with lipase-catalyzed transesterification for bio-diesel production
AUTHOR(S): Li, Lilin; Du, Wei; Liu, Dehua; Xu, Yuanyuan
CORPORATE SOURCE: Department of Chemical Engineering, Tsinghua University, Beijing, 100084, Peop. Rep. China
SOURCE: Shipin Yu Fajiao Gongye (2006), 32(5), 5-8
CODEN: SPYYDO; ISSN: 0253-990X
PUBLISHER: Shipin Yu Fajiao Gongye
DOCUMENT TYPE: Journal
LANGUAGE: Chinese

AB Acetate Me could be used as a novel acyl acceptor in the enzymical route for bio-diesel production, with which lipase expresses good stability. Acetate Me was adopted directly as a solvent to extract the oil from rapeseed powder and then the mixture of crude rapeseed oil and Me acetate was transesterified by lipase for bio-diesel production Three extraction factors (solvent weight, extraction time, extraction temperature) were studied by orthogonal test. Under the optimized conditions, the extraction rate could reach 51%, just as high as that with n-hexane as the extracting solvent, while the PLs content of the oil extracted by Me acetate was only 0.038%, much lower than that with n-hexane as the extracting solvent (PLs has been demonstrated to have some neg. effect on lipase activity). Extracted oil was transesterified with acetate Me catalyzed by lipase to produce bio-diesel and a bio-diesel yield of 92% could be achieved at 12 h reaction.

L4 ANSWER 4 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2007:1152916 CAPLUS
DOCUMENT NUMBER: 148:36089
TITLE: Enzymatic transesterification of olive oil and its precursors
AUTHOR(S): Coggon, Robert; Vasudevan, Palligarnai T.; Sanchez, Fernando

CORPORATE SOURCE: Department of Chemical Engineering, University of New Hampshire, Durham, NH, 03824, USA
SOURCE: Biocatalysis and Biotransformation (2007), 25(2-4), 135-143
CODEN: BOBOEQ; ISSN: 1024-2422
PUBLISHER: Informa Healthcare
DOCUMENT TYPE: Journal
LANGUAGE: English

AB The effect of different solvents and three different acyl acceptors on the transesterification of triolein (as a model compound) was investigated. The yield of biodiesel (Me or Et ester) was monitored as a function of time. The yield of the product was also determined in a solvent-free system for two different modes of stirring. The results indicate that the highest yield is obtained in a solvent-free system with mech. stirring. Me acetate is also effective as a solvent and acyl acceptor. Biodiesel was also produced by transesterification of triglycerides (triolein) present in olive oil with methanol and Novozym 435. The effect of the molar ratio of methanol to triolein, mode of methanol addition, enzyme activity and reaction temperature on overall conversion and yield was determined The final conversion and yield of biodiesel after a reaction time of 24 h were unaffected by changes in these parameters over the range studied. Preliminary findings indicate that the results obtained from small scale reactors and fresh oil can be extended to larger reactors and used oil.

REFERENCE COUNT: 12 THERE ARE 12 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 5 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2007:514630 CAPLUS
DOCUMENT NUMBER: 149:13249
TITLE: Improving enzymatic transformation of waste edible oil to biodiesel by adding organic base
AUTHOR(S): Chen, Zhi-feng; Zong, Min-hua; Wu, Hong
CORPORATE SOURCE: Lab of Applied Biocatalysis, South China University of Technology, Guangzhou, 510640, Peop. Rep. China
SOURCE: ACS Symposium Series (2007), 959(Ultraclean Transportation Fuels), 51-57
CODEN: ACSMC8; ISSN: 0097-6156
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English

AB The transesterification of waste edible oil and Me acetate to biodiesel catalyzed by the immobilized lipase Novozym 435 was explored. Novozym 435 could catalyze the transesterification of waste oil with high free fatty acid (FFA) content (≤27.8%) and Me acetate, and Me ester (ME) yield reached 77.5% after a reaction time of 24 h, which was much lower than that with refined corn oil being the raw material (86.2%). FFA was demonstrated to be the major influential factor on the reaction, ME yield dropped sharply with increasing FFA concentration Acetic acid, the byproduct formed in the transesterification of FFA with Me acetate, was found to be responsible for the decrease of ME yield. Addition of organic base trihydroxymethyl aminomethane and triethylamine at the concentration of 5% based on oil weight to the reaction system could not only speed up the reaction, but

improve ME yield.
REFERENCE COUNT: 7 THERE ARE 7 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 6 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2006:1165163 CAPLUS
DOCUMENT NUMBER: 146:524717
TITLE: Lipase-mediated conversion of vegetable oils into biodiesel using ethyl acetate as acyl acceptor
AUTHOR(S): Modi, Mukesh Kumar; Reddy, J. R. C.; Rao, B. V. S. K.; Prasad, R. B. N.
CORPORATE SOURCE: Division of Lipid Science and Technology, Indian Institute of Chemical Technology, Hyderabad, 500 007, India
SOURCE: Bioresource Technology (2006), Volume Date 2007, 98(6), 1260-1264
CODEN: BIRTEB; ISSN: 0960-8524
PUBLISHER: Elsevier B.V.
DOCUMENT TYPE: Journal
LANGUAGE: English
AB Et acetate was explored as an acyl acceptor for immobilized lipase-catalyzed preparation of biodiesel from the crude oils of Jatropha curcas (jatropha), Pongamia pinnata (karanj), and Helianthus annuus (sunflower). The optimum reaction conditions for interesterification of the oils with Et acetate were 10% of Novozym-435 (immobilized Candida antarctica lipase B) based on oil weight, Et acetate to oil molar ratio of 11:1 and the reaction period of 12 h at 50°. The maximum yield of Et esters was 91.3%, 90%, and 92.7% with crude jatropha, karanj, and sunflower oils, resp., under the above optimum conditions. Reusability of the lipase over repeated cycles in interesterification and ethanolysis was also investigated under standard reaction conditions. The relative activity of lipase could be well maintained over twelve repeated cycles with Et acetate while it reached to zero by the sixth cycle when ethanol was used as an acyl acceptor.
REFERENCE COUNT: 19 THERE ARE 19 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 7 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2006:1052001 CAPLUS
DOCUMENT NUMBER: 146:299006
TITLE: Application of silica aerogel encapsulated lipases in the synthesis of biodiesel by transesterification
AUTHOR(S): Orcaire, Olivier; Buisson, Paulette; Pierre, Alain C.
CORPORATE SOURCE: Institut de Recherches sur la Catalyse, CNRS-UPR 5401, Universite Claude Bernard-Lyon I, Villeurbanne, Fr.
SOURCE: Journal of Molecular Catalysis B: Enzymatic (2006), 42(3-4), 106-113
CODEN: JMCEF8; ISSN: 1381-1177
PUBLISHER: Elsevier B.V.
DOCUMENT TYPE: Journal
LANGUAGE: English
AB Two types of com. lipases prepns., one from Burkholderia cepacia, the other one from Candida antartica, were encapsulated in silica aerogels reinforced with silica quartz fiber felt and dried by the CO2

supercrit. technique. These immobilized biocatalysts were applied in biodiesel synthesis by transesterification of sunflower oil with Me acetate. They were efficient even with mixts. of both substrates without any solvent addition The aerogel encapsulation technique made it possible to maintain the enzymes in a dispersion state similar to the dispersion prevailing in an aqueous solution, even for further use in organic hydrophobic media. In transesterification in excess isooctane, the two lipases encapsulated in aerogels made from 40% MTMS, have activities relatively close to each other and comparable with com. Novozyme 435. On the other in transesterification with mixture of oil and Me acetate without any solvent, the kinetics were severely limited by substrate diffusion inside the aerogels. This was particularly true with the C. antartica, so that the corresponding aerogel encapsulated enzyme was much less active than com. Novozyme 435, although it improved after a few tests.
REFERENCE COUNT: 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

=> d l4 8-14 ibib abs

L4 ANSWER 8 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2006:345019 CAPLUS
DOCUMENT NUMBER: 144:491788
TITLE: Method for producing biodiesel by enzyme -catalyzed transesterification of high-acid-number waste oils
INVENTOR(S): Zong, Minhua; Chen, Zhifeng; Wu, Hong
PATENT ASSIGNEE(S): South China University of Technology, Peop. Rep. China
SOURCE: Faming Zhuanli Shenqing Gongkai Shuomingshu, 8 pp. CODEN: CNXXEV
DOCUMENT TYPE: Patent
LANGUAGE: Chinese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
CN 1730613	A	20060208	CN 2005-10036639	20050819
CN 1325606	C	20070711		
PRIORITY APPLN. INFO.:			CN 2005-10036639	20050819

AB The method includes placing C2-6 short-chain aliphatic esters and high-acid number waste oils at a molar ratio of (8-24):3 into a reactor; mixing uniformly; adding (based on oil weight) 5-30% lipase and 5-15% alkaline substance; and reacting on a vibrating bed at 30-60° for 8-48 h, wherein the alkaline substance is selected from triethylamine, potassium carbonate, etc.

L4 ANSWER 9 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2006:331929 CAPLUS
DOCUMENT NUMBER: 145:422251
TITLE: Transesterification of waste oil with high acid value to biodiesel catalyzed by immobilized lipase
AUTHOR(S): Chen, Zhifeng; Wu, Hong; Zong, Minhua
CORPORATE SOURCE: College of Biological Sciences and Biotechnology, South China University of Technology, Guangzhou,

Guangdong, 510640, Peop. Rep. China
SOURCE: Cuihua Xuebao (2006), 27(2), 146-150
CODEN: THHPD3; ISSN: 0253-9837
PUBLISHER: Kexue Chubanshe
DOCUMENT TYPE: Journal
LANGUAGE: Chinese
AB The transesterification of waste oil with high acid value and Me acetate to biodiesel catalyzed by the immobilized lipase Novozym 435 was explored. Novozym 435 can catalyze this reaction, and the Me ester (ME) yield reaches 77.5% after reaction for 24 h, which is much lower than that (86.2%) using refined corn oil as the raw material. The effects of water, free fatty acid, and acetic acid in the reaction system on the reaction were systematically studied. Water has little influence on the reaction when its content is lower than 0.05%, while above this value both the ME yield and the reaction rate decrease with increasing water content. Free fatty acid influences the reaction greatly, and the ME yield drops sharply with increasing free fatty acid concentration Acetic acid, the byproduct formed in the transesterification of free fatty acid with Me acetate, is responsible for the decrease of ME yield. The addition of organic bases such as trihydroxymethyl aminomethane and triethylamine at a concentration of 10% based on the oil mass to the reaction system can not only speed up the reaction, but improve the ME yield as well, with ME yields being 85.9% and 80.8%, resp., after reaction for 12 h. The operational stability of Novozym 435 is improved markedly by the addition of bases. Adding trihydroxymethyl aminomethane and triethylamine to the reaction system leads to a retention of 97% and 93% of the original activity of Novozym 435, resp., after operation of 10 batches, while the control is only 86%.

L4 ANSWER 10 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2005:844270 CAPLUS
DOCUMENT NUMBER: 143:308992
TITLE: Improving enzymatic transformation of waste edible oil to biodiesel by adding organic base
AUTHOR(S): Chen, Zhi-feng; Zong, Ming-hua; Wu, Hong
CORPORATE SOURCE: Biotechnology Department, South China University of Technology, Guangzhou, 510640, Peop. Rep. China
SOURCE: Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry (2005), 50(2), 809-810
CODEN: PSADFZ; ISSN: 1521-4648
PUBLISHER: American Chemical Society, Division of Fuel Chemistry
DOCUMENT TYPE: Journal; (computer optical disk)
LANGUAGE: English
AB The transesterification of waste edible oil and reformed corn oil was performed with Me acetate and lipase B from Candida Antarctica (Novozym 435), in order to produce biodiesel. The reaction rate and the fatty acid Me ester yield were improved by the addition of organic bases such as tri-hydroxymethyl aminomethane, triethylamine or pyridine.
REFERENCE COUNT: 7 THERE ARE 7 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 11 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2005:391617 CAPLUS
DOCUMENT NUMBER: 142:449357
TITLE: Method for preparing biodiesel from animal or plant

oil
INVENTOR(S): Du, Wei; Xu, Yuanyuan; Liu, Dehua
PATENT ASSIGNEE(S): Tsinghua University, Peop. Rep. China
SOURCE: Faming Zhuanli Shenqing Gongkai Shuomingshu, 10 pp.
CODEN: CNXXEV
DOCUMENT TYPE: Patent
LANGUAGE: Chinese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
CN 1436834	A	20030820	CN 2003-119600	20030313
WO 2004081158	A1	20040923	WO 2004-CN51	20040115
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
US 20060257986	A1	20061116	US 2006-549336	20060620
PRIORITY APPLN. INFO.:			CN 2003-119600 A	20030313
			WO 2004-CN51 W	20040115

AB Biodiesel was prepared by transesterification of animal or plant oil (castor oil, rapeseed oil, soybean oil, or fish oil) with short chain ester (such as Me acetate and Et acetate) at a molar ratio of 1:3-20 in the presence of lipase Novozyme 435 (30% of oil) at 20-60° for 4-20 h.

L4 ANSWER 12 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2005:174218 CAPLUS
DOCUMENT NUMBER: 142:462336
TITLE: Study on the kinetics of enzymatic interesterification of triglycerides for biodiesel production with methyl acetate as the acyl acceptor
AUTHOR(S): Xu, Yuanyuan; Du, Wei; Liu, Dehua
CORPORATE SOURCE: Department of Chemical Engineering, Tsinghua University, Beijing, 100084, Peop. Rep. China
SOURCE: Journal of Molecular Catalysis B: Enzymatic (2005), 32(5-6), 241-245
CODEN: JMCEF8; ISSN: 1381-1177
PUBLISHER: Elsevier B.V.
DOCUMENT TYPE: Journal
LANGUAGE: English

AB A new route for biodiesel production using Me acetate instead of methanol as the acyl acceptor was proposed in our previous research, and it has been found that this novel route could enhance the stability of the immobilized lipase greatly. In this paper, the kinetics of lipase -catalyzed interesterification of triglycerides for biodiesel production with Me acetate as the acyl acceptor was further studied. First, a simplified model based on Ping Pong Bi Bi with substrate competitive inhibition mechanism was proposed to describe the reaction kinetics of the

interesterification. During our further study, it was observed that three consecutive and reversible reactions occurred in the interesterification of triglycerides and Me acetate. So, a kinetic model based on mass balance of three second-order reversible reactions was developed and the reaction rate constant, k, was determined by solving the differential rate equations of the reaction system. The results showed that kDG-MG (0.1124) and kMG-TA (0.1129) were much higher than kTG-DG (0.0311), which indicated that the first step reaction was the limit step for the overall interesterification.

REFERENCE COUNT: 9 THERE ARE 9 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 13 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2004:558567 CAPLUS
DOCUMENT NUMBER: 141:313005
TITLE: Comparative study on lipase-catalyzed transformation of soybean oil for biodiesel production with different acyl acceptors
AUTHOR(S): Du, Wei; Xu, Yuanyuan; Liu, Dehua; Zeng, Jing
CORPORATE SOURCE: Department of Chemical Engineering, Tsinghua University, Beijing, 100084, Peop. Rep. China
SOURCE: Journal of Molecular Catalysis B: Enzymatic (2004), 30(3-4), 125-129
CODEN: JMCEF8; ISSN: 1381-1177
PUBLISHER: Elsevier Science B.V.
DOCUMENT TYPE: Journal
LANGUAGE: English

AB Me acetate, a novel acyl acceptor for biodiesel production has been developed, and a comparative study on Novozym 435-catalyzed transesterification of soybean oil for biodiesel production with different acyl acceptors was conducted and reported in this paper. Methanol has a serious neg. effect on enzymic activity. A molar ratio of methanol to oil of above 1:1 leads to serious inactivation of the enzyme. However, when Me acetate was used as the acyl acceptor, a yield of 92% of Me ester could be obtained with a molar ratio of Me acetate to oil of 12:1, and Me acetate showed no neg. effect on enzymic activity. Addnl., with crude soybean oil as the oil source and methanol as acyl acceptor, a much lower Me ester yield was obtained than that with refined soybean oil, while with Me acetate as acyl acceptor, an equally high yield of Me ester (92%) was achieved for both soybean oils. Lipase loses its activity very rapidly during repeated expts. with methanol as the acyl acceptor, while there is almost no detected loss in lipase activity, even after being continuously used for 100 batches, when Me acetate was used for biodiesel production Moreover, the byproduct triacetin is an important chemical with a higher value than glycerol, and this novel acyl acceptor seems very promising for lipase-catalyzed large-scale production of biodiesel.

REFERENCE COUNT: 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 14 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2003:603489 CAPLUS
DOCUMENT NUMBER: 139:383869
TITLE: A novel enzymatic route for biodiesel production from renewable oils in a solvent-free medium

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AUTHOR(S):              Xu, Yuanyuan; Du, Wei; Liu, Dehua; Zeng, Jing
CORPORATE SOURCE:       Department of Chemical Engineering, Tsinghua
                        University, Beijing, 100084, Peop. Rep. China
SOURCE:                 Biotechnology Letters (2003), 25(15), 1239-1241
                        CODEN: BILED3; ISSN: 0141-5492
PUBLISHER:              Kluwer Academic Publishers
DOCUMENT TYPE:          Journal
LANGUAGE:               English
AB   A new enzymic route for biodiesel production from soybean oil was
     developed using Me acetate as a novel acyl acceptor.
     Novozym 435 (immobilized Candida antarctica lipase) gave the
     highest Me ester (ME) yield of 92%.  The optimum conditions of the
     transesterification were 30% enzyme based on oil
     weight; a molar ratio of Me acetate/oil of
     12:1; temperature 40° and reaction time 10 h.  Since no glycerol was
     produced in the process, this method is very convenient for recycling the
     catalyst and byproduct triacetylglycerol showed no neg. effect on the
     fuel property.
REFERENCE COUNT:        9     THERE ARE 9 CITED REFERENCES AVAILABLE FOR THIS
                              RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT


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     (FILE 'HOME' ENTERED AT 09:59:01 ON 18 SEP 2008)

     FILE 'CAPLUS' ENTERED AT 09:59:39 ON 18 SEP 2008
L1         2441 S (?ESTERIFICATION) (L) ((METHYL (A) ACETATE) OR (ETHYL (A) ACE
L2          177 S L1 (L) (FAT# OR OIL#)
L3           27 S L2 AND (LIPASE OR ENZYME)
L4           14 S L3 AND FUEL

=> s l1 (L) (fatty (a) acid (a) alkyl (a) ester)
        409031 FATTY
            14 FATTIES
        409035 FATTY
                  (FATTY OR FATTIES)
       4673506 ACID
       1651424 ACIDS
       5190793 ACID
                  (ACID OR ACIDS)
        617705 ALKYL
          6723 ALKYLS
        620746 ALKYL
                  (ALKYL OR ALKYLS)
        628504 ESTER
        461618 ESTERS
        872282 ESTER
                  (ESTER OR ESTERS)
L5           3 L1 (L) (FATTY (A) ACID (A) ALKYL (A) ESTER)

=> d l5 1-3 ibib abs

L5   ANSWER 1 OF 3  CAPLUS  COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER:       2008:464894  CAPLUS
TITLE:                  Biodiesel production by supercritical process with
                        crude bio-methanol prepared by wood gasification
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AUTHOR(S): Isayama, Yohei; Saka, Shiro
CORPORATE SOURCE: Department of Socio-Environmental Energy Science, Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto, 606-8501, Japan
SOURCE: Bioresource Technology (2008), 99(11), 4775-4779
CODEN: BIRTEB; ISSN: 0960-8524
PUBLISHER: Elsevier Ltd.
DOCUMENT TYPE: Journal
LANGUAGE: English

AB In order to prepare a genuine biodiesel, it is essential to use methanol prepared from biomass but not natural gas for biodiesel production Thus, we have proposed to use crude bio-methanol produced by wood gasification for biodiesel production Since such a bio-methanol contains some impurities, an effect of its impurities was studied on the biodiesel production by supercrit. method. In general, impurities in crude bio-methanol are reported to include Me formate, ethanol, 1-butanol, diisopropyl ether, water, etc. Triglycerides and oleic acids were, thus, treated with these impurities under supercrit. conditions. As a result, it was found that Me formate, ethanol and 1-butanol could convert them to fatty acid alkyl esters (BDF), whereas no conversion was achieved with diisopropyl ether. Thus, crude bio-methanol can be used for BDF production as a substitute for methanol from fossil resources. However, due to more efficient reaction, crude bio-methanol can be more applicable to the two-step supercrit. methanol process, consisting of hydrolysis of triglycerides and subsequent esterification of fatty acids, compared with the one-step supercrit. methanol process, where transesterification of triglycerides is a major reaction.

REFERENCE COUNT: 16 THERE ARE 16 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2007:435952 CAPLUS
DOCUMENT NUMBER: 146:421640
TITLE: Method for production of fatty acid alkyl ester as biodiesel fuel
INVENTOR(S): Saka, Shiro
PATENT ASSIGNEE(S): Kyoto University, Japan
SOURCE: PCT Int. Appl., 59pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2007043567	A1	20070419	WO 2006-JP320295	20061011

W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW
RW: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BW, GH,

GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM

JP 2007106689	A	20070426	JP 2005-298162	20051012
JP 2007131595	A	20070531	JP 2005-327942	20051111
JP 2007169173	A	20070705	JP 2005-365631	20051219

PRIORITY APPLN. INFO.: JP 2005-298162 A 20051012
JP 2005-327942 A 20051111
JP 2005-365631 A 20051219
OTHER SOURCE(S): CASREACT 146:421640; MARPAT 146:421640
AB A process to improve the efficiency of the production of a fatty acid alkyl ester, which is useful as biodiesel fuel, is described. A fatty acid alkyl ester can be produced by performing esterification between a fatty acid and a carboxylic acid ester under predetd. temperature/pressure conditions (step X). The fatty acid may be produced from a raw oil-and-fat material or a free fatty acid contained in the raw oil-and-fat material through a given process. The given process to be performed prior to the step X may comprises a step of performing transesterification between a fatty acid glyceride contained in the raw oil-and-fat material and a carboxylic acid under predetd. temperature/pressure conditions to yield the desired fatty acid (step A) or a step of hydrolyzing a fatty acid glyceride contained in the raw oil-and-fat material under predetd. temperature/pressure conditions to yield the desired fatty acid (step B). Thus, a 1:15 mixture of Me formate and oleic acid was heated at 350° for 9 min in a batch reactor under critical conditions to give 93.4% Me oleate. Various esterification conditions were examined using rapeseed oil, methanol (transesterification to give fatty acid esters), Me formate or Et formate, and acetic acid (transesterification to give fatty acids) as well as solubility of reaction mixts. in organic solvent.
REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 3 OF 3 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2000:464963 CAPLUS
DOCUMENT NUMBER: 133:89231
TITLE: Method for preparation of α-sulfo fatty acid alkyl ester salts
INVENTOR(S): Tano, Tetsuo; Yamauchi, Azusa; Nishio, Hiroshi; Matoba, Seiji; Yoshiya, Masahisa
PATENT ASSIGNEE(S): Lion Corp., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 7 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2000191626	A	20000711	JP 1998-371658	19981225

PRIORITY APPLN. INFO.: JP 1998-371658 19981225
OTHER SOURCE(S): CASREACT 133:89231; MARPAT 133:89231
AB A process for preparation of RCH2CH(SO3H)CO2R1 salts (R = C6-24 linear or

branched alkyl or alkenyl; R1 = C1-6 linear or branched alkyl) involves sulfonation of fatty acid alkyl esters represented by formula RCH2CH2CO2R1 (R, R1 = same as above) and esterification of the resulting crude sulfonic acids with lower alcs., wherein the latter esterification step is carried out by adding lower alcs. and C2-6 fatty ether. This process esterified fatty acid ester-SO3 (1:2) adducts (impurities), i.e. RCH2CH(SO3H)CO2-SO2-OR1 using lower alcs. to RCH2CH(SO3H)CO2R1 and provides α-sulfo fatty acid alkyl ester salts of improved purity which are light-colored and reduced in odor and are useful as surfactants. Thus, 7 volume% anhydrous SO3(g) in N was introduced into a 2:8 weight mixture of Me myristate and Me palmitate (iodine value of 0.40) in a 1/1.2 molar ratio of fatty acid ester/SO3 at 80° over 60 min and the resulting mixture was stirred at 80° for 30 min to give crude α-sulfo fatty ester Me ester containing diadduct impurities (98.0% reaction ratio for the fatty acid Me esters). A MeOH solution containing di-Me ether 10, Me acetate 1, and H2O 0.1 weight% and H2O2 were added to the crude α-sulfo fatty Me ester in 20 and 2.5 weight part of the MeOH solution per 100 part α-sulfo fatty acid Me ester, followed by adding 2.5 weight part H2O2. The resulting mixture was stirred at 80° for 155 min for esterification and bleaching and neutralized by aqueous NaOH to pH 7-8 followed by stripping residual alc. on a evaporation dish to give a 67.5 weight% solution of α-sulfo fatty acid Me ester sodium salt,. The latter solution showed slight odor and remained the same after one month, and odor can be masked by perfume.

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     (FILE 'HOME' ENTERED AT 09:59:01 ON 18 SEP 2008)

     FILE 'CAPLUS' ENTERED AT 09:59:39 ON 18 SEP 2008
L1          2441 S (?ESTERIFICATION) (L) ((METHYL (A) ACETATE) OR (ETHYL (A) ACE
L2           177 S L1 (L) (FAT# OR OIL#)
L3            27 S L2 AND (LIPASE OR ENZYME)
L4            14 S L3 AND FUEL
L5             3 S L1 (L) (FATTY (A) ACID (A) ALKYL (A) ESTER)

=> s alcoholysis (L) ((methyl (a) acetate) or (ethyl (a) acetate) or formate or
propionate)
          7694 ALCOHOLYSIS
       1069165 METHYL
           717 METHYLS
       1069597 METHYL
                 (METHYL OR METHYLS)
        979707 ME
         11297 MES
        986913 ME
                 (ME OR MES)
       1699369 METHYL
                 (METHYL OR ME)
        573680 ACETATE
         30105 ACETATES
        586084 ACETATE
                 (ACETATE OR ACETATES)
        505356 ETHYL
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           43 ETHYLS
       505382 ETHYL
                (ETHYL OR ETHYLS)
       690323 ET
         8598 ETS
       697316 ET
                (ET OR ETS)
      1054585 ETHYL
                (ETHYL OR ET)
       573680 ACETATE
        30105 ACETATES
       586084 ACETATE
                (ACETATE OR ACETATES)
        44864 FORMATE
         3678 FORMATES
        46235 FORMATE
                (FORMATE OR FORMATES)
        50853 PROPIONATE
         2073 PROPIONATES
        51923 PROPIONATE
                (PROPIONATE OR PROPIONATES)
L6        116 ALCOHOLYSIS (L) ((METHYL (A) ACETATE) OR (ETHYL (A) ACETATE) OR
              FORMATE OR PROPIONATE)

=> s 16 (L) (fat# or oil#)
       324865 FAT#
       970002 OIL#
L7         14 L6 (L) (FAT# OR OIL#)

=> s 17 (L) (fatty (a) acid (a) alkyl (a) ester)
       409031 FATTY
           14 FATTIES
       409035 FATTY
                (FATTY OR FATTIES)
      4673506 ACID
      1651424 ACIDS
      5190793 ACID
                (ACID OR ACIDS)
       617705 ALKYL
         6723 ALKYLS
       620746 ALKYL
                (ALKYL OR ALKYLS)
       628504 ESTER
       461618 ESTERS
       872282 ESTER
                (ESTER OR ESTERS)
L8          0 L7 (L) (FATTY (A) ACID (A) ALKYL (A) ESTER)

=> s 17 and fuel
       446610 FUEL
       177049 FUELS
       501158 FUEL
                (FUEL OR FUELS)
L9          0 L7 AND FUEL

=> s 17 and (fatty (a) acid (a) methyl (a) ester)
       409031 FATTY
```

```
            14 FATTIES
         409035 FATTY
                (FATTY OR FATTIES)
        4673506 ACID
        1651424 ACIDS
        5190793 ACID
                (ACID OR ACIDS)
        1069165 METHYL
            717 METHYLS
        1069597 METHYL
                (METHYL OR METHYLS)
         979707 ME
          11297 MES
         986913 ME
                (ME OR MES)
        1699369 METHYL
                (METHYL OR ME)
         628504 ESTER
         461618 ESTERS
         872282 ESTER
                (ESTER OR ESTERS)
           5186 FATTY (A) ACID (A) METHYL (A) ESTER
L10           0 L7 AND (FATTY (A) ACID (A) METHYL (A) ESTER)

=> d his

     (FILE 'HOME' ENTERED AT 09:59:01 ON 18 SEP 2008)

     FILE 'CAPLUS' ENTERED AT 09:59:39 ON 18 SEP 2008
L1         2441 S (?ESTERIFICATION) (L) ((METHYL (A) ACETATE) OR (ETHYL (A) ACE
L2          177 S L1 (L) (FAT# OR OIL#)
L3           27 S L2 AND (LIPASE OR ENZYME)
L4           14 S L3 AND FUEL
L5            3 S L1 (L) (FATTY (A) ACID (A) ALKYL (A) ESTER)
L6          116 S ALCOHOLYSIS (L) ((METHYL (A) ACETATE) OR (ETHYL (A) ACETATE)
L7           14 S L6 (L) (FAT# OR OIL#)
L8            0 S L7 (L) (FATTY (A) ACID (A) ALKYL (A) ESTER)
L9            0 S L7 AND FUEL
L10           0 S L7 AND (FATTY (A) ACID (A) METHYL (A) ESTER)

=> d l7 1-7 ibib abs

L7   ANSWER 1 OF 14  CAPLUS  COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER:         1981:588695  CAPLUS
DOCUMENT NUMBER:          95:188695
ORIGINAL REFERENCE NO.:   95:31499a,31502a
TITLE:                    Effect of quality of pentaerythritol on alkyd resin
                          and its paint
AUTHOR(S):                Liu, Zhuangli
CORPORATE SOURCE:         Chengchow Paint Co., Chengchow, Peop. Rep. China
SOURCE:                   Tuliao Gongye (1981), 61, 4-7
                          CODEN: TLKYD5; ISSN: 0253-4312
DOCUMENT TYPE:            Journal
LANGUAGE:                 Chinese
AB   The color of pentaerythritol (I), the content of impurities, and the
     content of dipentaerythritol (II)  [126-58-9] or polypentaerythritol
     affected the synthesis, color, and transparency of alkyd resins.  I having
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a dark color gave a dark color alkyd resin. II was controlled at .apprx.10%, increasing content of II rapidly increased the viscosity during esterification. Sodium formate [141-53-7] accelerated the alcoholysis of I and vegetable oils, but darkened the resin color and increased turbidity.

L7 ANSWER 2 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1965:411080 CAPLUS
DOCUMENT NUMBER: 63:11080
ORIGINAL REFERENCE NO.: 63:1994c-e
TITLE: Examination of "mono" and technical pentaerythritols and the effect of its impurities on the formulation and properties of alkyds
AUTHOR(S): Thirkel, E.R.
SOURCE: Chim. Peintures (1964), 27(12), 363-8
DOCUMENT TYPE: Journal
LANGUAGE: French
AB The analysis of .apprx.20 com. samples of pentaerythritol (I) is reported; samples containing >97% I and <0.06% ash are classified as "monopentaerythritol" (II), while those containing <96% I, 0.1-0.5% ash, and 3.5-12.4% dipentaerythritol (III) are classified as tech. I. The effect of impurities on color, clarity, alcoholysis and esterification in the manufacture of alkyds with an oil/resin ratio of 65-70% is discussed. A Ca formate content of 0.002-0.004% in I is considered as an allowable limit for maximum gloss and clarity. Linseed oils containing >0.001% Ca gave rise to turbidity in alkyds (measured by comparison with an infusorial earth suspension in H2O, suitably colored with a solution of I); <0.2% Na formate (calculated as Na2O) gives no turbidity but frothing during the monoglyceride formation. CaSO4, Na2SO4 and traces of SiO2 are not harmful. Fe in I rarely exceeds 0.01%; >0.2% Fe formate darkens the color. Traces of inorg. acids leads to the appearance of insol. particles in the resin. The alcoholysis of linseed oil-I-phthalic anhydride alkyds at 265° is catalyzed to a greater extent by Na formate than by Ca formate. Esterification is accelerated by Na formate in tech. I, in contrast to the general opinion attributing such an effect to the high % of III in tech. I. At 230-80° II forms the monoglyceride without the appearance of gelified particles. A conductometric method for the determination of the final point of alcoholysis is more practical than the conventional MeOH tolerance method. By replacing tech. I by II it is possible to reduce the excess of I by 2% and the oil/resin ratio by 0.5%. Alkyds with an oil/resin ratio of 69% can be prepared by saving 8% of II and with no excessive increase in the acid number; drying, pigment-wetting, and film properties are satisfactory. The use of II of low Ca formate content is recommended for alkyds of better color and reproducibility.

L7 ANSWER 3 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1963:59612 CAPLUS
DOCUMENT NUMBER: 58:59612
ORIGINAL REFERENCE NO.: 58:10147e-h,10148a-c
TITLE: 5-Substituted β-(2-furyl)propionic acid esters. Synthesis from β-furfurylideneketones and their hydrogenation
AUTHOR(S): Thewalt, Klaus; Rudolph, Walter
CORPORATE SOURCE: Chem. Werke Witten, Wirten/Ruhr, Germany
SOURCE: Chemische Berichte (1963), 96, 136-42

CODEN: CHBEAM; ISSN: 0009-2940
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 58:59612

AB The alcoholysis of furfurylideneacetophenone (I) gives good yields of the esters of 3-(5-phenyl-2-furyl)propionic acid (II). This reaction was applied to a series of analogs of I. The hydrogenation of the resulting esters over Raney Ni yields γ-substituted γ-butyrolactones, and over Cu chromite catalyst, ω-substituted alkanediols. Several tech. interesting reactions of the lactones and the diols are described. I (230 g.) in 750 g. BuOH containing 1.5% HCl stirred 24 h. at 100° under N and distilled gave 130 g. yellow, crude ester which was purified by hydrogenation at 100°/20-5 atmospheric over Raney Ni to yield pure Bu ester (III) of II, b2 175-80°, m. 14°, n20D 1.5552. III (5.00 g.) saponified with aqueous alc. KOH gave 4.00 g. II, needles, m. 117° (H2O). III (20 g.) and 5% H2SO4 refluxed 2 h. and filtered gave 11 g. BzCH2CH2COCH2CH2CO2H, m. 113-14° (H2O). Furfurylideneacetone (1.5 g.) treated in the usual manner with BuOH, and the resulting pale yellow Bu ester (IV) of 3-(5-methyl-2-furyl)propionic acid (V) saponified with KOH gave 0.80 g. V, needles, m. 56° (H2O). 1-Benzylidene-3-furfurylideneacetone (60 g.) in 240 cc. absolute BuOH and 50 cc. dry CHCl3 added during 3 h. dropwise with stirring at 100° to 330 cc. absolute BuOH containing 1.8% HCl and evaporated after an addnl. 3-4 h., and the black, oily residue distilled yielded 18 g. Bu 3-(5-styryl-2-furyl)propionate (VI), b0.8 191-2°. III (300 g.) in MeOH hydrogenated at 150°/85 atmospheric over Raney Ni gave 55 %forerun, b1, 150-4.5°, and 120 g. tetrahydrofuryl analog (VII) of VI, b1 155-55.5°, n20D 1.5008; the forerun containing up to 20% γ-phenylpropyl-γ-butyrolactone (VIII) saponified, acidified, boiled with Ba(OH)2.8H2O, filtered, and worked up yielded an addnl. 110 g. VII. VII (25 g.) and 2N KOH refluxed 2 h., acidified, and extracted with Et2O gave 13 g. 3-(5-phenyl-2-tetrahydrofuryl)propionic acid (IX), b1 183-5°, n20D 1.5270, m. 32-3° (after 3 mo); S-(p-bromobenzyl)isothiuronium salt m. 126-7°. IX (3 g.) refluxed with 0.9 equivalent Ba(OH)2 in H2O and evaporated, and the residue extracted with Et2O yielded 2.5 g. Ba salt of IX. III (20 g.) in MeOH hydrogenated over Pd-C yielded 14.5 g. VIII, b0.6 152-4°, n20D 1.4772. VIII (5.0 g.) and 3.5 g. Ba(OH)2.8H2O refluxed 3 h. in H2O, evaporated, and worked up gave 6.5 g. Ph(CH2)3CH(OH)CH2CH2CO2H. IV (10 g.) in MeOH hydrogenated over 1 g. Pd-C yielded 6.5 g. γ-butyl-γ-butyrolactone, b4 106-7°, n20D 1.4476. III (200 g.) in dioxane hydrogenated at 200°/250 atmospheric over 20 g. Cu chromite catalyst gave a small forerun of 2-(3-phenylpropyl)tetrahydrofuran (X), and 130 g. Ph(CH2)3CH(OH)(CH2)3OH (XI), b1 169-70°, needles, m. 42°, n20D 1.5126, d26 1.014; bis(phenylurethane), glass; diacetate b0.6 146-8°, n20D 1.4658. XI (25 g.) and 5 g. dry Al2O3 stirred 3 h. at 170° and extracted with Et2O yielded 14 g. X, b1 105-7°, n20D 1.5142. XI (250 g.) and 1000 g. polyphosphoric acid stirred 1 h. at 100-10°, poured into an equal volume H2O, and extracted with Et2O gave 160 g. 3-(1,2,3,4-tetrahydro-1-naphthyl)propanol, b2 143-4°, n20D 1.5480, d20 1.047; phenylurethane m. 232-4°; 3,5-dinitrobenzoate, yellowish-tinted, m. 81-2°; Ph3C ether, yellowish-tinted glass. III (5.0 g.) in 50 cc. dry Et2O added dropwise with stirring to 1.5 g. LiAlH4 in 150 cc. dry Et2O and worked up after 20 min. gave 2.8 g. 3-(5-phenyl-2-furyl)propanol,

yellowish viscous oil, b0.8 142-4°, n20D 1.5859; phenylurethane, slightly yellowish-tinted, m. 80° (petr. ether). VIII (150 g.) in dioxane hydrogenated at 250°/250 atmospheric over Cu chromite gave 60 g. 7-cyclohexylcycloheptanol (XII), b0.8 119-20° [phenylurethane, needles, m. 221-3° (decomposition); 3,5-dinitrobenzoate m. 78°], and 57 g. XI, b0.8 155-7°, n20D 1.4700, d20 0.900. XII (10 g.) added dropwise to 12 g. CrO3 in AcOH, refluxed 2 h., and extracted with Et2O yielded 7.0 g. 7-cyclohexylheptanoic acid, b3 164-8°, m. 26°. XI (200 g.) in dioxane hydrogenated at 190°/200 atmospheric over Raney Ni gave 85% 7-cyclohexylheptane-1,4-diol, b1 160-2°, m. 33°, n30D 1.4798.

L7 ANSWER 4 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1961:13559 CAPLUS
DOCUMENT NUMBER: 55:13559
ORIGINAL REFERENCE NO.: 55:2711b-i,2712a-h
TITLE: An alkaloid of Dioscorea hispida, Dennstedt. VI. Some investigations on the synthesis of 2-tropanone
AUTHOR(S): Davies, W. A. M.; Jones, J. B.; Pinder, A. R.
CORPORATE SOURCE: Univ. Coll., Cardiff, UK
SOURCE: Journal of the Chemical Society (1960) 3504-12
CODEN: JCSOA9; ISSN: 0368-1769
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
AB cf. CA 53, 18076c. Possible routes for the synthesis of (±)-2-tropanone (I) were explored. 2-Isobutyl-N,N-dimethylcycloheptylamine (II) was synthesized, probably as a mixture of cis- and trans-forms. II was not identical with the fully hydrogenated Hofmann base from dioscorine. Dioscorinol (III) separated as rhombic prisms, m. 119-20° (C6H6). Ozonolysis of III gave 2β-acetonyl-2α-tropanol (IV), isolated as the picrate, prisms, m. 120° (MeOH). IV (1 g.) kept 24 hrs. with 65 cc. 0.1N NaOH, cooled, saturated with K2CO3, continuously extracted 16 hrs. with Et2O, and distilled gave 0.55 g. I, b14 98°, b17 105-6°, [α]24D 15.0° (c 1.43, H2O); picrate used to give pure I, b14.5 100°. I (0.3 g.) in 15 cc. 2N HCl added to 50 mg. PtO2 prereduced in 10 cc. 2N HCl, the mixture treated with 2 cc. concentrated HCl, the mixture shaken 18 hrs. with H, extracted with Et2O, and distilled gave 0.25 g. tropane, b92 96°; picrate m. 284-5° (decomposition). Et α-bromocrotonate (5 g.) added dropwise with cooling to 6.07 g. Et methylaminoacetate during 15 min., the mixture kept overnight at room temperature, treated with Et2O, and distilled gave 4.3 g. Et N-ethoxycarbonylmethyl-γ-methylaminocrotonate (V), b0.1 95-6°. V (1.56 g.) in 15 cc. alc. shaken 1 hr. with H over PtO2 gave 0.2 g. Et N-ethoxycarbonylmethyl-γ-methylaminobutyrate (VI), b10 134-5°. The alc. distillate contained Et butyrate. A similar result was obtained in attempts to effect the hydrogenation in the presence of Pd-C. VI (by Dieckmann cyclization, followed by acid hydrolysis and decarboxylation) afforded 1-methyl-3-oxopiperidine, b11 56-8°; MeI derivative, prisms, m. 200-2° (decomposition). MeNH2 and acrylonitrile gave β-(methylamino)propionitrile. Alcoholysis gave Et β-(methylamino) propionate. The ester (17.4 g.) and 11.1 g. Et bromoacetate kept overnight at room temperature gave N-(β-ethoxycarbonylethyl)-N-ethoxycarbonylmethylmethylamine (VII), b0.15 74°. Cyclization of VII gave 1-methyl-3-oxopyrrolidine, b21 48-9°; methiodide m. 234° (decomposition). Na salt of 2-hydroxymethylenetropinone (2 g.) heated 10 min. in 10 cc. AcOH with 1.1

g. PhNHMe gave 1.4 g. 2-(methylanilinomethylene)tropinone (VIII), rhombic prisms, m. 121-2° (Me2CO). Attempts to reduce VIII to 2-(methylanilinomethylene)tropane or 2-(methylanilinomethylene)tropine under a variety of conditions were unsuccessful. Dehydration of tropine with AcOH-H2SO4 gave tropidine (IX). Trifluoroacetic anhydride (40 g.), obtained by dehydrating the acid with P2O5, added dropwise during 15 min. to 5.6 g. 86% H2O in 83 cc. CH2Cl2, the mixture stirred 15 min. at 0°, dried 0.5 hr., and filtered gave trifluoroperacetic acid (X). IX (5 g.) added to 9.45 g. CF3CO2H in 33 cc. MeCN, then X added (10 min.), the mixture kept 4 days at 0°, the solvents removed, the oil dissolved in 30 cc. CH2Cl2, the solution treated with 5 g. anhydrous Na2SO4 then 30 g. K2CO3, stirring continued 4 hrs., the solution decanted, the residue washed with CH2Cl2, and evaporated gave 4.86 g. brown oil. Fractionation in vacuo gave 0.3 g. IX, followed by 1.63 g. 2β,3β-epoxytropane (XI), b6 93-4°. Attempts to liberate XI from its salt by use of NEt3 or Amberlite were unsuccessful. XI picrate m. 255° (decomposition). Attempts to prepare XI by treatment of IX or tropidine trifluoroacetate with X in the presence of anhydrous Na2CO3 gave IX N-oxide; picrate, yellow needles, m. 255-6.5° (decomposition). Reduction of the oxide with SO2 gave IX and on catalytic reduction gave tropane; picrate m. 285°. The action of HCO3H on IX formate gave principally the unchanged base, accompanied by a little 2β,3α-tropane-diol (XII). XI (2.08 g.) in 30 cc. Et2O added to 0.28 g. LiAlH4 in 30 cc. Et2O during 15 min., the mixture left 16 hrs. at room temperature, decomposed, the solution decanted, and distilled gave 1.62 g. (±)-2-β-tropanol (XIII), b18 94-5°; picrate m. 263-3.5° (decomposition). Attempts to oxidize XIII to (±)-isomer of I with CrO3 were unsuccessful. In one or two expts., a small yield of crystalline material was obtained, m. 140°. Hydrolysis with NaOMe in MeOH 2 days at room temperature gave XII. It was concluded that the product was either 2β-acetoxy-3α-tropanol or 3α-acetoxy-2β-tropanol. In one experiment, IX was detected in the product. (CF3CO)2O (6.3 g.) added during 10 min. to 1 g. 86% H2O2 in 40 cc. CH2Cl2, the mixture stirred 15 min. at 0°, the solution added during 10 min. to IX trifluoroacetate (from 2.5 g. IX) in 20 cc. MeCN, the mixture refluxed 0.5 hr., set aside overnight, evaporated, the sirup dissolved in H2O, saturated with K2CO3, and extracted 24 hrs. with Et2O gave 1.3 g. XII, rhombic prisms, m. 101°; MeI salt, prisms, m. above 320°; picrate, yellow needles, 208-10° (decomposition). Attempts to dehydrate XII with 20% H2SO4 or KHSO4 resulted in recovery of XII. XII (1.93 g.) with 0.7 cc. AcOH and 1.5 cc. concentrated H2SO4 heated 5 hrs. at 165° gave 1.52 g. (±)-2β,3α-tropane-diol (XIV), m. 103.5-5.0° (ligroine). A small yield of tropinone was also obtained; picrate m. 219°. SOCl2 (2 cc.) added dropwise to 0.61 g. XIV, the mixture stirred 0.5 hr. at room temperature, refluxed 18 hrs., and extracted with Et2O-CH2Cl2 gave 0.33 g. 3-chlorotropidine, b0.1 52-4°. IX (5 g.) in 50 cc. H2O at 0° treated with 4.35 g. KMnO4 and 8.7 g. MgSO4.7H2O in 435 cc. H2O during 5 hrs., stirred 1 hr., cooled, extracted 30 hrs. with Et2O in the presence of 500 g. KOH, and the extract concentrated gave unchanged IX. The remaining oil extracted with ligroine and evaporated gave 0.40 g. XIV; picrate, yellow rhombs, m. 239.5-40.5° (decomposition). IX (0.47 g.) in 10 cc. Et2O left 2 days at room temperature with 1

g. OsO_4 in 20 cc. Et_2O, the osmic ester collected, dissolved in 50 cc. H_2O, refluxed 0.5 hr. with 6 g. Na_2SO_3 in H_2O, saturated with K_2CO_3, and extracted 48 hrs. with Et_2O gave 0.5 g. XIV. XIV (0.36 g.) heated 6 hrs. at 120° with 3 cc. concentrated H_2SO_4 gave 0.18 g. tropinone, b18 104°; picrate m. 219°. Isovaleronitrile (by refluxing isobutyl bromide, KCN, and 60% alc.) (20 g.) refluxed 45 min. with 350 cc. alc. during addition of 33 g. Na, acidified, evaporated, the residual aqueous solution basified, and extracted gave 14 g. residual isopentylamine, b. 96-7°. Isopentylurethan, prepared by condensation of the amine and $ClCO_2Et$ in quant. yield, b14 106-7°. The urethan (40 g.), 100 cc. Et_2O, 100 g. $NaNO_2$, 30 g. ice, and 140 cc. H_2O mixed and shaken 1 hr. below 15°, accompanied by the addition of 66 cc. concentrated HNO_3 and 100 cc. H_2O, gave 46 g. isopentyl-N-nitrosourethan (XV). Cyclohexanone (25.5 g.), 30 cc. MeOH, and 0.6 g. anhydrous Na_2CO_3 treated during 1.5 hrs. with 46 g. XV and after 16 hrs. at room temperature distilled gave 27.3 g. product, b13-14 102-6°, purified by formation of 2-isobutylcycloheptanone semicarbazone (XVI), plates, m. 131-2° (50% aqueous MeOH). Hydrolysis of XVI by heating with aqueous $(CO_2H)_2$ furnished 16.5 g. 2-isobutylcycloheptanone (XVII), b12-13 104-5°; 2,4-dinitrophenylhydrazone, plates, m. 76°. XVII (15 g.) in 20 cc. MeOH mixed with NH2OH.AcOH in MeOH, the mixture refluxed 0.5 hr., evaporated, and the oil taken up in Et_2O gave 14.6 g. 2-isobutylcycloheptanone oxime (XVIII), b11-12 140-1°. XVIII (6.8 g.) in 100 cc. Et_2O added during 0.5 hr. to 2.5 g. $LiAlH_4$ in 150 cc. Et_2O, after 24 hrs. at room temperature the solution refluxed 3 hrs., cooled, decomposed, and fractionated gave 5.1 g. 2-isobutylcycloheptylamine (XIX), b15 124°. XIX (2 g.), 3 g. 90% HCO_2H, and 3 g. 40% HCHO mixed in the cold, heated 3 hrs., 15 cc. dilute HCl added, and the mixture extracted with Et_2O gave 2 g. II, b15 114°; MeI derivative, softening at 85°, m. 102-5°. Infrared spectra were given for a number of the above compds.

L7 ANSWER 5 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:	1960:10940 CAPLUS
DOCUMENT NUMBER:	54:10940
ORIGINAL REFERENCE NO.:	54:2158f-i,2159a-i,2160a-f
TITLE:	Reductones. XII. The synthesis of acetoacetic ester-1-C14 and α,β-dioxobutyric acid ester-1-C14
AUTHOR(S):	Dahn, H.; Hauth, H.
CORPORATE SOURCE:	Univ. Basel, Switz.
SOURCE:	Helvetica Chimica Acta (1959), 42, 1214-24 CODEN: HCACAV; ISSN: 0018-019X
DOCUMENT TYPE:	Journal
LANGUAGE:	German

AB cf. C.A. 52, 13717g. Ethyl acetoacetate-1-C14 (I) was prepared in two ways: MeCN + $BrCH_2C_1^4O_2Et$ (II) + Zn → I-1-C14 in 46% yield, 99.5% of the activity remaining in the 1-position; and AcCl + $CH_2(C_1^4O_2Et)(CO_2R)$ → $AcCH(C_1^4O_2Et)(CO_2R)$, where R = $CHMe_2$ or CH_2Ph, and the CO_2R group removed to produce I-1-C14. The reaction of I-1-C14 with HNO_2 to give the 2-isonitroso compound, which was decomposed by N_2O_4, yielded $AcCOC_1^4O_2Et$ (III). Mol. wts. indicated that the hemihydrate of III was a dimer, and although the ultraviolet data showed two CO groups, indicating an open chain 1-3 diol, the pH depression by HBO_3 suggested a cyclic, cis-1,2-diol. Thus, $BrCH_2CO_2H$-1-C14 (1 mc./millimole) was esterified with

diazoethane in ether and the crude II-1-C14 diluted with inactive ester. Etched and dried Zn wool (15.5 g.) was stirred and heated 75 min. with 20 g. diluted II-1-C14, 31.1 ml. dry MeCN, 20 ml. absolute C6H6, and 10 ml. absolute ether. The solution was heated an addnl. 2.5 hrs. under reflux, cooled, 80 ml. ice-cold 2N H2SO4 added, the organic phase separated, washed with water and 2N NaHCO3, dried, and distilled on the water bath. Distillation of the residue gave 71.4 g. I-1-C14, b10 66-8°, average sp. mol. BaCO3 activity after dilution with 11.88 g. inactive I 4.948 ± 0.035 + 105. I-1-C14 was decarboxylated with EtOH and 2N H2SO4 1.5 hrs. at 80° and the CO2 absorbed as BaCO3, sp. mol. activity 4.926 ± 0.023 + 105, indicating 98.7% retention of activity in the carboxyl group. I-1-C14 (120.2 mg.) in 0.5 ml. EtOH and 4 ml. 2N H2SO4 was decarboxylated 2.5 hrs. at 80°, cooled, neutralized with 4 ml. 2N NaOH, and 124 mg. semicarbazide-HCl and 189 mg. Na acetate-3H2O added. After 5 hrs. the product was dried at 25°C in vacuo. The residue was extracted with MeOH, evaporated, and crystallized from water to yield 82 mg. crystals, m. 186-8°, of acetone semicarbazone. The sp. mol activity was 0.033 + 105 and after two more crystns. was 0.018 + 105. A solution of 34.8 ml. dry Et acetate, 20 g. II, 20 ml. absolute benzene, and 10 ml. absolute ether was added dropwise during 1.5 hrs. with heating and rapid stirring to 15.5 g. Zn wool, then heated 4 hrs. under reflux, and finally cooled in ice, and 75 ml. 2N H2SO4 added. After treating as above, 4.31 g. I (28% yield), b10 66-8°, was obtained. The yield of I was less if the Zn-II compound was prepared first (7%) or if II was added to the mixture of Et acetate and Zn (16%), or if AcOH was used instead of H2SO4 (19%). Control reactions showed that Zn and Et acetate alone produced only 3% I. A solution of 51.8 ml. PhCH2OH in 40.4 ml. absolute pyridine was added during 2 hrs. at 20° with stirring to 37.8 ml. ClCH2COCl, then heated 2 addnl. hrs., the mixture extracted with water and ether, the ether layer washed with 2N H2SO4 and 2N NaHCO3, dried, and distilled to give 87.7 g. ClCH2CO2CH2Ph (IV), b0.4 84-6°, n22D 1.5220. NCCH2CO2Et (15 ml.) and 75 ml. PhCH2OH heated 2 hrs. at 195-205° and the alcs. removed in vacuo gave 28.8 g. NCCH2CO2CH2Ph (V), b0.02 95°, n25D 1.5173, nitrile band at 4.44 μ, ester band at 5.73 μ, and C:C band at 6.24 μ (liquid film). V could not be obtained from IV and KCN. V (22.6 g.) in 7.52 ml. absolute EtOH treated with dry HCl 4 hrs. at 0°, allowed to crystallize 36 hrs. at -5°, filtered, washed with ether and pentane, and dried gave 31.6 g. leaves, m. 88-90° (decomposition). The crystals were shaken 4 hrs. with ice water, neutralized with Na2CO3, and extracted with ether. Removal of the ether gave 71% ethyl benzyl ester of malonic acid (VI), b0.3 110°, n26D 1.4922, ester bands at 5.75 μ and C:C bands at 6.22 μ (liquid film). K (3.91 g.) was dissolved in 60 ml. absolute tert-BuOH and the excess tert-BuOH distilled VI (11.11 g.) in 20 ml. absolute ether was added and the mixture heated 15 min. under reflux. After addition of 30 ml. absolute ether, a solution of 14.2 ml. AcCl in 15 ml. absolute ether was added at 0° with stirring during 1 hr., the mixture stirred 2 hrs. at 22°, and finally heated 30 min. under reflux. The mixture was cooled, treated with ice water extracted with ether, the ether solution washed with 2N KHCO3, dried, and distilled The residual oil (VII) was dissolved in 75 ml. absolute Et acetate, 1.5 g. Pd-C added, and hydrogenated 35 min., 1.078 l. H being absorbed. The solution was filtered, the solvent evaporated, and the residue distilled in vacuo. The fraction, b10 60-100°, was dissolved in 20 ml. 0.5N absolute EtOH-HCl,

and allowed to stand 12 hrs. at 22°, and finally distilled first at atmospheric pressure, and then at 66-8°/10 mm. to yield 3.67 g. I. The crude VII was dissolved in ether, cooled, extracted rapidly with ice-cold N NaOH, and the ether solution washed with water. After drying and distillation of the ether the residual oil b0.1 147-9°, n25D 1.5033, vinyl ester bands at 5.68 μ, ester bands at 5.82 μ, and C:C bands at 6.05 μ (liquid film), no longer showed the FeCl3 reaction, and was identified as O-Ac derivative of enolacetylmalonic acid ethyl ester benzyl ester (VIII). Acidification of the NaOH extract, extraction with ether, and distillation at 80-95°/0.4 mm. gave (apparently) acetylmalonic acid ethyl ester benzyl ester, λ 3.1 to 4.2 μ (associated OH), 5.7-5.9 μ (ester), 6.12 μ (C:C), and 6.24 μ (phenyl) (liquid film), and a red FeCl3 reaction. ClCH2CO2H tert-Bu ester (60.2 g.), 13.0 g. KCN in 160 ml. tert-BuOH, 25 ml. water, and a trace of NaI was heated 5 hrs. at 90°, then concentrated in vacuo, extracted with ether, the ether solution washed with water, 2N HCl, and 2N KHCO3, and dried. Removal of ether and distillation in vacuo gave 18.6 g., b. 42-6°, and 4.3 g., b. 94.7°. The first fraction was redistd. at 86-8°/12 mm. to give 18.5 g. cyanoacetic acid tert-butyl ester (IX), d21 1.0095, n21D 1.4172, b. 107-8, λ 4.40 μ (nitrile) and 5.74 μ (ester) (liquid film). The second fraction redistd. at 90-2° gave a colorless oil, n22D 1.4312, recrystd. from MeOH-water to leaflets, m. 58-9°, λ (Nujol) 4.41 μ (nitrile) and 5.74 μ (ester), apparently cyanosuccinic acid di-tert-Bu ester. IX could not be prepared by alcoholysis of malonic acid ethyl tert-Bu ester, also, cyanoacetic acid Et ester did not react with tert-BuOH. K (3.91 g.) in 60 ml. absolute tert-BuOH and 10 ml. absolute ether was treated at 22° with 7.06 g. IX in 20 ml. absolute ether, then diluted with 100 ml. absolute ether, and stirred at -10° 2 hrs. with dropwise addition of 14.2 ml. acetyl chloride in 20 ml. absolute ether. Ice water was added, the ether phase separated, washed with water, and dried. Evaporation of the ether and distillation of the residue gave 1.25 g. cyanoacetoacetic acid tert-Bu ester (X), and 6.83 g. O-acetyl derivative of enol of cyanoacetoacetic acid tert-Bu ester (XI), b. 87-9°, d24 1.0657, n24D 1.4542, λ 233 mμ (log ε 4.02) (EtOH), λ 4.49 μ (α,β-unsatd. nitrile), 5.60 μ (vinyl ester), 5.78 μ (α,β-unsatd. ester), and 6.14 μ (C:C) (liquid film). XI (5.72 g). in 20 ml. acetone was treated with 15 ml. 2N KHCO3 with gas evoln. After 2 hrs. shaking at 22° the solution was acidified, extracted with ether, washed, and distilled in vacuo to give 4.25 g. X, b0.2 57-9°, leaflets from pentane, m. 44-6°, λ 195 mμ (log ε 3.84) and 253.5 mμ (log ε 4.07) (EtOH), broad band at 3.5 μ, and bands at 4.51 μ, 6.05 μ (β-oxo ester, enolic), 6.22 μ (conjugated C:C) (CH2Cl2), red coloration with FeCl3. I-1-C14 (17.08 g.) and 13.6 g. NaNO2 treated dropwise during 45 min. with 50 ml. 4N H2SO4 at 0°, stirred 2 hrs., then diluted with 40 ml. water and extracted with ether, the ether phase washed with water and 2N NaHCO3, and dried gave an ether solution of isonitrosoacetoacetic ester-1-C14 (XII). During 4 hrs. XII-1-C14 was treated with 11 ml. N2O4, the solution held overnight at 0°, and finally 2 days at 22° with warming and gas evolution. The ether was removed and the residue distilled to give 7.87 g. oil, which was dissolved in water, shaken with CaCO3, and extracted with ether to give 5.69 g. III-1-C14, yellow oil, b10

64-6°, after three distns., sp. molar activity 4.908 ± 0.030 + 105. For comparison, inactive III b12 68°, n20D 1.4135, λ 190 mμ (log ε 3.19) and 420 mμ (log ε 1.30) (cyclohexane), λ 5.72 μ and 5.78 μ (diketone) (CH_2Cl_2). III-1-C14 and 0.5 mole water crystallized from $CHCl_3$ and dried 15 hrs. at 22° over $CaCl_2$ gave needles, m. 94-5°. Mol. weight detns. in camphor and Exalton gave values of 230, in acetone 226. III-1-C14 had in water λ 188 mμ (log ε 3.39), 219 mμ (log ε 2.63), 288 mμ (log ε 2.00), in EtOH λ 195 mμ (log ε 3.18), 221.5 mμ (log ε 2.61), 289 mμ (log ε 1.98), in CH_2Cl_2 λ 2.84 μ (OH), 5.75 μ (C:O), in Nujol λ 2.83 and 3.01 μ (associated OH) and 5.72, 5.76 and 5.82 μ (C:O functions). Direct oxidation of I with SeO_2 in boiling dioxane yielded 29% crude III. I in Ac_2O with gaseous N_2O_3 at 20° gave 11% III, with liquid N_2O_4 at 20° 17% III. Pure XII in ether, with N_2O_3 at 20° gave 11% III, with N_2O_4 28% III. XII with HCHO-HCl at 20° gave 17% III. α-Hydroxyacetoacetic ester, b12 93-6°, n19D 1.4340, red $FeCl_3$ test in EtOH, decolorized dichlorophenol-indophenol immediately and was oxidized with a slight excess of $FeCl_3$ in water at 20° to give 30% III. III (72 mg.) in 3 ml. water was treated with 60 mg. o-phenylene-diamine in 1.5 ml. EtOH and heated to 100° 5 min. with the addition of one drop 2N HCl. On cooling, 102 mg. needles, m. 73-3.5°, of 3-methylquinoxazoline-2-carboxylic acid ethyl ester separated For C14 determination the labeled substance in weighed portions, corresponding to 30 mg. $BaCO_3$, was oxidized with CrO_3 to CO_2, converted to $BaCO_3$, and filtered. The dry $BaCO_3$ layer was smoothed with a polished steel die and counted directly.

L7 ANSWER 6 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1954:51432 CAPLUS
DOCUMENT NUMBER: 48:51432
ORIGINAL REFERENCE NO.: 48:9107h-i,9108a-b
TITLE: Oil-modified alkyd resins
INVENTOR(S): Gourley, Samuel; Purvis, John E. B.
PATENT ASSIGNEE(S): Imperial Chemical Industries Ltd.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 697318		19530923	GB 1950-6343	19500314

AB In the manufacture of oil-modified alkyd resins, catalytic Ca salts of fatty acids are precipitated in fine dispersion during esterification and produce a haze. By addition of dibasic acids, the precipitate is flocculated and can be removed to produce a clear haze-free product. Dibasic acids such as oxalic, malonic, succinic, adipic, or sebacic acid are used to precipitate the Ca salts. For example, 3000 parts of alkali-refined linseed oil (I) is heated to 240° with stirring under CO_2. In 90 min., 534 parts of pentaerythritol (II) containing Ca formate equivalent to 0.1% CaO is added. The mixture is maintained at 240° during these addns. and for 4 1/2 hrs. more. The II melts and reacts with I forming a homogeneous liquid consisting mainly of an ester. The fatty acid radical

of I esterifies one OH group of the glycerol and the II. The product is cooled to 90-95° and 2.9 parts H2C2O4 are added to give a flocculent precipitate When alcoholysis is substantially complete, 1107 parts of C6H4(CO)2O and 102 parts of II with the same Ca formate content as before are added. The mixture is heated to 200° until its acid value falls to < 10. The resulting melt is perfectly clear and free from haze. Another formula contains 2750 g. of I and 870 g. of glycerol with 2.5 g. of Ca(OAc)2. Phthalic acid or its anhydride, with or without maleic anhydride, are used for esterification of an incompletely esterified polyhydric alc. composition prepared by alcoholysis of a fatty oil with one or more polyhydric alcs. With sebacic acid, the cooled alcoholysis product is centrifuged before esterification with phthalic anhydride.

L7 ANSWER 7 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1952:28420 CAPLUS
DOCUMENT NUMBER: 46:28420
ORIGINAL REFERENCE NO.: 46:4813c-f
TITLE: Synthetic drying oils
PATENT ASSIGNEE(S): N. V. de Bataafsche Petroleum Maatschappij
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
NL 68954		19511115	NL	

AB Polymers of allyl-type alcs. (I), which are prepared from polymeric esters of allyl alcs. or these polymeric esters (II) themselves are brought into reaction with unsatd. fatty acids (III), their anhydrides or halides (cf. Dutch patent 68,281). I may be prepared from II by hydrolysis in the presence of a Cu compound as a catalyst or by alcoholysis preferably with the same allyl-type alc. as is present in the polymer, since such a selection enables a monomeric ester, which may be directly subjected to polymerization, to be recovered. I may consist of one or more kinds of allyl alcs. while representatives of I containing 3 to 10 monomer units are preferred. Instead of the raw polymers there may be used polymers which are air-blown, hydrogenated, or treated with SO2. It is advantageous to use III with at least 16 C atoms and a iodine number (Wijs) of at least 120, such as palmitoleic, linolenic, arachidonic, clupadonic, licanic acids, etc. The acids may be prepared by isomerization, dehydration, dehydrogenation, or synthesis, or may be obtained from natural oils, tall oil, or waxes. The reaction between I and III may be carried out in solution, preferably in the presence of a catalyst, with continuous removal of H2O and under a blanket of an inert gas. The drying oils obtained, which may be purified, decolorized by a treatment with acid or alkali, bleached and bodied by heating, preferably in the presence of O at a temperature between 38 and 260°, are preferably used in the presence of 0.01 to 1.0% by weight of a usual drier. Drying is also promoted by O-liberating compds. The oils, which are color-stable at room temperature, may be used in the manufacture of paint and lacquer, and for sizing, resp., impregnating fibrous material. In an example, 9 parts of polyethyl alloxy formate were heated with 14 parts linseed fatty acids at 270° for 10 min. and at 300° for 30 min. A pale yellow drying oil having an acid number of 57 was obtained.

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L7 ANSWER 8 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1949:45539 CAPLUS
DOCUMENT NUMBER: 43:45539
ORIGINAL REFERENCE NO.: 43:8210d-i,8211a-f
TITLE: Organic cyclic silicon condensation polymers
INVENTOR(S): Hersh, Joseph M.
PATENT ASSIGNEE(S): Continental Oil Co.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2464231		19490315	US 1945-600239	19450618

GI For diagram(s), see printed CA Issue.

AB Monomeric cyclic silicon compds. have been condensed to form cyclic silicon condensation polymers (I) by improved methods and the resulting polymers used in numerous compns. I may be prepared from silicon dihalides or disilicon halides. E.g. CH2.CH2.CH2.CH2.CH2.SiCl2 (II) is prepared by stirring in a reaction flask with a reflux condenser 2.5 mols. Mg chips and 5-10 vols. anhydrous ether (on the halide used) and adding 1 mol. 1,5-dibromopentane at first slowly and undild., then more rapidly with anhydrous ether diluent. The reaction may require warming to start, or the addition of a reaction promoter, such as iodine or EtI. During the reaction an even ether reflux should be maintained for 3 hrs. by cooling. To the Grignard compound which seps. as an oily bottom layer is added slowly with rapid stirring and sharp cooling 1 mol. SiCl4 in ether solution, the reaction product is decanted from the solids and fractionally distilled; essentially pure II is collected at 165-175°. The hydrolysis of II to the primary cyclic silicone (III) where n is not more than 5 is carried out by dissolving II in 2-3 vols. C6H6, adding gradually to ice-water or ice-brine, extracting with C6H6 and vacuum distillation of the solvent. III may be further condensed by dissolving in a noncondensable hydrocarbon solvent and treating with an acid-acting chemical condensing agent (IV), such as H2SO4, HSO3Cl, HSO3F, H3PO4, H4P2O7, HPO3, P2O5, P2S5, PCl3, PCl5, ZnCl2, CoCl2, MnCl2, FeCl3, AlCl3, AlBr3, HF, BF3, or HI. The time of exposure of III to IV dets. the degree of condensation. At the optimum polymeric structure the condensable mass is freed of IV and inhibited from further condensation by storage at low temps., or solution in a noncondensing hydrocarbon medium, or by the addition of a condensation inhibitor (V), such as EtOH, iso-PrNH2, certain ethanolamines, Et silicate, Et borate, PhOH, p-NH2C6H4OH, N-tert-butyl-p-aminophenol, Ph silicate, or Et acetate in amts. from 1 to 10%. V must be removed prior to use of the condensed III. Many monomeric cyclic silicon compds. are listed which will undergo the above reactions producing stable, homogeneous silicones of 500 to 10,000 mol. weight Disilicon halides may be prepared as follows: "chloro dicyclobutyl silico ether" (VI) is prepared by treating 1 mol. silicon oxychloride and 5 mols. Mg in anhydrous ether with 1,4-dichlorobutane to complete reaction, distilling off the ether and the crude VI. VI is not purified but is hydrolyzed rapidly in ice-water, washed to remove HCl producing primary dicyclobutyl silicol ether (VII) which has 2 hydroxyl

groups per mol. This may be further condensed to give the condensed dicyclic silicone. VII is a practically colorless, limpid liquid which, over concentrated H2SO4, gradually condenses giving off H2O, to form a more highly condensed cyclobutyl silicone. Direct preparation of polymeric cyclic silicones may be carried out by using active metals, such as Mg, Zn, Al, Na, Li, K, Li-Na alloy, or Na-K alloy. Thus p-dichlorobenzene in the presence of molten dispersed particles of metallic Na (10 molal parts) in toluene or xylene reacts instantaneously with silicon oxychloride to produce "chloro dicyclophenyl silicol ether" which may then be hydrolyzed in the same vessel to produce I. Cyclic silicon esters (VIII) may be prepared by alcoholysis of the corresponding halogenated compds., such as VI. VIII are not readily hydrolyzed by H2O and may be stored for considerable periods of time. Before condensation VIII is treated with constant-boiling Hl to produce a controlled condensate. Many uses are described for the polymers. The compds. (I) may be used as untifoam agents in blended heavy-duty oils, as antifrothing agents in oily-organic processing systems, such as vacuum distillation of lubricating-oil stocks, dehydration of oils, and soap formation in the neutralization of fatty and organic acids. In certain lubricating compns. concns. of the condensed cyclic silicones of 0.1-10% may act as viscosity-improving and stabilizing agents. Halogen-bearing silicones have excellent extreme-pressure and load-carrying properties in these lubricants. When addnl. quantities of halogens are introduced in the cyclic silicon compound structure the resulting compds. form an extremely viscous, tough, thermotropic composition of high resistance to ignition and attack by insects or fungi; they are useful as fire-proofing, fungus- and-insect-proofing components of impregnating or coating baths for fabrics, ropes, organic plastics, wood, etc. The higher polymeric forms of I are useful for elec. insulation, coating, etc.

L7 ANSWER 9 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1949:36595 CAPLUS
DOCUMENT NUMBER: 43:36595
ORIGINAL REFERENCE NO.: 43:6627f-i,6628a-i,6629a-i,6630a-i,6631a
TITLE: Condensation reactions of N-substituted pyridones
AUTHOR(S): Adams, Roger; Schrecker, Anthony W.
SOURCE: Journal of the American Chemical Society (1949), 71, 1186-95
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 43:36595

AB The activity of the 6-Me group in 1-substituted 2-pyridones was studied as an aid in the synthesis of cytisine. Carbethoxymethyl groups gave compds. similar to β-keto esters and cyanomethyl groups compds. similar to β-carbonylated nitriles. These compds. formed Na enolates reacting with acyl and alkyl halides (cf. Kaslow and Cook, C.A. 40, 871.2). 2-Amino-6-methylpyridine (I) (108 g.) in 111 cc. H2SO4 and 830 cc. H2O was diazotized with 73 g. NaNO2 in 140 g. H2O at 5°, stirred 1 h. below 10°, then heated to 90°, 205 g. K2CO3 added, the mixture evaporated on the steam bath, and the residue extracted with boiling C6H6, concentrated to 500 cc., and cooled to give 101 g. 6-methyl-2(1H)-pyridone (II), m. 158-9°, b. 282°. Boiling diazotized I (108 g.) was neutralized with Ba(OH)2.8H2O 568 in boiling H2O 1500 g., 50 cc. 25% NaOH added, and the filtrate concentrated to dryness; crystallization from 95% EtOH gave

115.5 g. of the Na derivative of 6-methyl-R (R = 2(1H)-pyridone throughout this abstract), m. 290°, very soluble in H2O, insol. in Et2O. To 98.7 g. II and 21 g. Na in 250 cc. warm MeOH, 130 g. Me2SO4 was added during 15 min. at room temperature; after 2 h.' refluxing, addition of 220 g. 25% aqueous NaOH, steam distillation to remove the byproduct 2-methoxy-R, filtration, and CHCl3 extraction gave 82 g. 1,6-dimethyl-R (III), b2 110°, m. 56.5-8° (from dry Et2O). Alkaline hydrolysis of the product from MeI and I gave only 23% III, and 2-picoline with Me2SO4, then alkaline ferricyanide, gave no III. III and dry HCl in Et2O gave the HCl salt, m. 202-3° (corrected) (from absolute EtOH), sublimes at 75° and 3 mm.; III picrate, m. 134-6° (from 95% EtOH). 4-Methyl-R (IV), prepared as II in 78% yield, with extraction by boiling EtOH, b12 186-7°, m. 130° (corrected) (from C6H6). 1,4-Dimethyl-R (V), prepared as III in 77% yield, b1 110°, m. 59°, somewhat deliquescent but less so than III. V.HCl, prepared in absolute EtOH with dry HCl, cooling, and addition of dry Et2O, m. 173-4°; V picrate m. 168-9°. Absolute EtOH (69 cc.) was cautiously added to 10.55 g. K covered with 60 cc. Et2O, the mixture refluxed to dissolve K, 39.5 g. anhydrous Et2C2O4 in 250 cc. Et2O added at room temperature, then after 10 min. 30.75 g. III with shaking. After 3 days the precipitated yellow K salt (VI) of VII (see below) was crystallized from absolute EtOH, m. 310-20° (decomposition), 94.7% yield. Crude VI (61.8 g.) in 27 g. H2SO4, and 450 g. H2O gave 42.8 g. Et 1-methyl-R-6-pyruvate (VII), m. 175-6° (from 95% EtOH). NaOEt prepared from NaH in Et2O and EtOH with the above procedure gave 95% VI and then 85% VII. This procedure gave no pyruvic esters with 2-picoline, II, or 2-acetamido-6-methylpyridine. Similarly 84% K salt (VIII) of IX was prepared; stirring 12 g. VIII in 5.25 g. H2SO4, 55 g. H2O, 30 g. chopped ice, and 100 cc. CHCl3, extraction with 50 cc. more CHCl3, addition of 3.5 cc. 28% NH4OH in 30 cc. H2O, further CHCl3 extraction, concentration of the extract to 49 cc., and addition of 200 cc. ligroin (b. 30-60°) gave 8.1 g. (79%) Et 1-methyl-R-4-pyruvate (IX), m. 157-8° (from Me2CO). Only 56% IX was obtained from VIII by the method used with VI. NaOEt condensation gave 65% IX. VII (2.23 g.) in boiling 22.3 g. 6% H2SO4 30 min. gave a precipitate which was filtered after several hrs. in the ice box and crystallized from H2O to give 1.78 g. 1-methyl-R-6-pyruvic acid (X), m. 239-40° (effervescence); 1-methyl-R-4-pyruvic acid (XI), 55% yield, and crystallized from 50% HOAc, m. 246° (effervescence). Addition of 3.3 cc. 30% H2O2 and 5 cc. H2O to 1.95 g. X in 18 cc. 10% NaOH solution below 0°, keeping 48 h. in the ice box, removing excess H2O2 with MnO2, chilling 1 h., acidifying with concentrated HCl to Congo red, several min.'s boiling, and further cooling gave 1.46 g. 1-methyl-R-6-acetic acid (XII), m. 188° (effervescence) (from H2O); XII heated at its m.p. gave CO2 and III; picrate, m. 134-6°. VII (0.446 g.), 3.6 cc. 10% NaOH, 0.7 cc. 30% H2O2, and 2 g. ice, 14 h. in the ice box, addition of 0.3 cc. 30% H2O2, and 14 more hrs.' chilling, etc., gave 0.18 g. XII. 1-Methyl-R-4-acetic acid (59% from XI), m. 184° (effervescence). VI (10.4 g.), 92 g. ice, and 14 cc. 30% H2O2 were chilled 1.5 h., 1.8 g. NaOH in 10 cc. H2O added, then, after 42 h.' chilling, MnO2, etc., gave 3.55 g. (58%) 1-methyl-R-4-carboxylic acid, tan crystals, purified by boiling a Na2CO3 solution with Darco, acidifying, and crystallizing from HOAc, m. 260° (cf. 247-8° of Spath and Koller, C.A. 17, 2712). Direct distillation gave 1-methyl-R; HgCl2 double salt, m. 127°. XII (0.55 g.), 14 cc. MeOH, and 0.5 cc. H2SO4 refluxed 2

h., addition of aqueous K2CO3, concentration of the CHCl3 extract, and addition of ligroin (b. 30-60°) gave 0.46 g. Me ester, m. 102°. XII (17.6 g.), 50 cc. EtOH, and 6 cc. H2SO4 refluxed 2 h., addition of 50 cc. C6H6, slow distillation of the steam bath to 0.5 volume, then concentration in vacuo to 110 cc., addition of K2CO3, etc., gave 18.3 g. Et ester (XIIa), m. 100-1°. XIIa did not condense with ArCHO and piperidine, or with Et2C2O4 and KOEt. VII (15 g.) and 15 g. H2NOH.HCl in 75 cc. C5H5N and 75 cc. absolute EtOH refluxed 4 h., concentration in vacuo, and trituration of the residue with 75 cc. cold H2O gave 13.8 g. Et 1-methyl-α-isonitroso-R-6- propionate (XIII), m. 198° (from 95% EtOH). XIII (8.91 g.) boiled in 45 cc. 2 N aqueous NaOH 80 min., cooled, and 9 cc. concentrated HCl added, gave 7.49 g. free acid (XIV), m. 182° (decomposition) (from 50% HOAc). XIV was also prepared in 91% yield by addition of 10.42 g. ice-cold H2NOH.HCl in 20 g. H2O to 19.5 g. X, 14.75 g. NaOH, and 60 g. H2O at 0°, filtration after 43 h. at 30°, and precipitation with 33 cc. concentrated HCl at 5°. XIV (19.1 g.) heated over a free flame gave much CO2, H2O, and 12.5 g. 1-methyl-R-6-acetonitrile (XV), b1 168°, as a yellow oil; crystallization from C6H6-Et2O and redistn. gave colorless needles, m. 95.5-6.5°. XV did not condense with Et2CO3, but with BzH and C5H5N or piperidine gave high yields of a yellow impure product, m. 260-2°; it could not be purified. XV in boiling dilute NaOH in EtOH 3 h. and acidification gave 86% XII. Addition of 0.69 g. XIIa, then 0.45 cc. PhCH2Cl, to 0.084 g. Na in 2 cc. EtOH, 21 h.' refluxing, addition of 0.2 cc. PhCH2Cl, 3 h.' refluxing (mixture now neutral), steam distillation, solution of the oil in the residue in Et2O, washing with dilute aqueous Na2CO3, concentration to 3 cc., addition of 30 cc. ligroin (b. 30-60°), and chilling gave 0.62 g. 1-methyl-α-benzyl-R-6-acetate, m. 104-5° (from 35% EtOH). Saponification of 0.74 g. in 1.0 g. NaOH, 2 g. H2O, and 5 g. EtOH, with 2 h.' refluxing, and precipitation with dilute HCl gave 0.59 g.; decolorizing with Darco in dilute NH4OH and repptn. gave the free acid (XVI), m. 155°. XVI heated in vacuo gave off CO2 at 150°, then heated at 180° 5 min., and distilled at 150° and 2 mm. it gave 1-methyl-6-phenethyl-R, m. 95.5-6.5°. XV (1.48 g.) and PhCH2Cl, etc., added (with 10 cc. C6H6) to NaOEt, extraction of the C6H6 layer with H2O, filtration through Darco, and addition of ligroin gave 1.0 g. 1-methyl-α-benzyl-R-6-acetonitrile, m. 132° (from dilute EtOH, then C6H6-Et2O); hydrolysis in 62% H2SO4 or preferably with KOH in EtOH-H2O gave XVI. Addition of 4.30 g. XIIa, then 3.5 cc. BuI, to 0.51 g. Na in 10 cc. EtOH, 24 h.' refluxing, concentration to dryness, addition of 20 cc. H2O, and Et2O extraction gave 3.6 g. Et 1-methyl-α-butyl-R-6-acetate (XVII), b2 159-60°, nD20 1.5180; the pale yellow oil gave colorless crystals in Dry Ice-Me2CO. Lower yields were obtained from BuBr. XVII (0.59 g.) and 33% aqueous NaOH (0.93 g.) were heated on the hot plate to give a solution, then 1 h. on the steam bath, diluted with 1 cc. H2O, 0.7 cc. concentrated HCl added at 0°, and the CHCl3 solution of the precipitated oil washed with H2O and concentrated; the residue gave CO2 at 150°, and, after 5 min. at 180°, was distilled below 1 mm. and

at 90° as 6-amyl-1-methyl-R, nD20 1.5250. Addition of 2.52 g. XIIa to NaOEt (from 0.31 g. NaH, 0.77 cc. EtOH, and 20 cc. Et2O), 15 min.'s refluxing, addition of 0.97 cc. AcCl in 10 cc. Et2O at 0°, keeping 5 min. at 0° and 2 h. at 35°, extraction with aqueous NaHCO3, and addition of ligroin (b. 30-60°) gave 1.16 g. crude liquid β-keto ester, solidifying at 6°. Refluxing 0.97 g. with 15 cc. concentrated HCl 22 h., concentration to a small volume, addition of excess saturated aqueous Na2CO3, concentration of the CHCl3 extract, trituration with ligroin, crystallization from C6H6, and distillation at 5 mm. and 150° bath temperature gave 0.18 g. 6-acetonyl-1-methyl-R, m. 136.5-7.5°; p-nitrophenylhydrazone, prepared by 30 min.'s refluxing in HOAc, m. 209-10° (blackening). III (2.1 g.), 2.58 g. 3-NO2C6H4CHO, and 1.77 g. Ac2O were heated 20 h. at 175-80°, the black oil treated 5 min. with boiling MeOH and 0.2 g. Norit, the MeOH removed by addition of 3 cc. concentrated HCl and 20 cc. H2O and boiling, the aqueous solution extracted with C6H6, boiled 2 min., made alkaline with aqueous 25% Na2CO3, and the precipitate repptd. from 2 cc. boiling EtOH with 30 cc. H2O and crystallized from C6H6-ligroin, then 95% EtOH, as 0.05 g. 1-methyl-6-(m-nitrostyryl)-R, m. 216-18°. Refluxing 15.0 g. 2-acetamido-6-methylpyridine (Seide, J. Russ. Phys.-Chemical Society 50, 534(1918)), 10.6 g. BzH, and 5.1 g. Ac2O 30 h., steam distillation, dilution of the residue with 250 cc. H2O, acidification with HCl, filtration through Celite and Norit, and addition of NH4OH gave a yellow oil; drying in Et2O, precipitation from CHCl3 solution with ligroin, solution in dilute HCl, and precipitation by addition of NH4OH with chilling, and precipitation from EtOH with H2O gave 2.94 g., crystallized from C6H6-ligroin and from 70% EtOH, of 6-acetamido-2-stilbazole (XVIII), m. 149-50°. XVIII (4.2 g.) boiled 3 h. in 6 N HCl and crystallized from EtOH gave 3.98 g. 6-amino-2-stilbazole-HCl, m. 249-52°; addition of NH4OH and crystallization from C6H6-ligroin (b. 90-110°) gave 96% free base (XIX), m. 110°. Addition of NaNO2 to XIX in warm dilute H2SO4, 5 min.'s boiling, addition of excess NH4OH, 2 min.'s boiling, solution of the precipitate in hot dilute aqueous NaOH, and buffering with CO2 repptd. 48% 6-hydroxy-2-stilbazole (or 6-styryl-R), m. 210-11° (from 95% EtOH). 2-Acetamido-4-methylpyridine (8.0 g.) (cf. Seide, C.A. 18, 2896), 6.3 g. BzH, and 2.7 g. Ac2O refluxed under N 46 h., addition of 15 cc. concentrated HCl, steam distillation of the dark oil, and extraction of the residue twice with 50 cc. boiling concentrated HCl gave a dark sticky residue (XX) and a clear yellow solution (XXI). XXI was boiled 3 h., diluted with 50 cc. H2O, boiled 4 h., cooled, the yellow flocculant precipitate dissolved in boiling EtOH, an excess of dilute NH4OH added, the tan precipitate boiled in 50 cc. concentrated HCl with Norit, filtered hot, diluted with 50 cc. hot H2O, then chilled 3 h., the precipitated product dissolved in 50 cc. hot EtOH, 4 cc. 28% NH4OH in 10 cc. EtOH added, then hot H2O to saturation, and the mixture chilled to give 1.52 g. 2-amino-4-stilbazole (XXII), m. 216-17° (from 95% EtOH). XX was digested with Me2CO at

0°, then with boiling concentrated HCl, dissolved in 70 cc. boiling EtOH, and the solution heated with 40 cc. concentrated HCl; slow dilution with 100 cc. boiling H2O gave a yellow precipitate, repptd. from boiling EtOH with NH4OH as 0.29 g. microcrystals, m. 234-5°, containing C 84.26, H 5.59 and N 6.87%, but of unknown structure. XXII (2.4 g.) in 1.5 cc. concentrated H2SO4 and 10 cc. HOAc was chilled in ice-salt and precipitated as the sulfate; diazotization with gradual addition of 1.0 g. NaNO2 in 2 g. H2O at 0°, addition of more NaNO2 at room temperature (to a pos. starch iodide test), precipitation with 100 cc. H2O, addition of excess NH4OH to the mixture at 90°, and crystallization from 95% EtOH gave 0.86 g. 2-hydroxy-4-stilbazole (or 4-styryl-R), m. 238-9°. Heating an intimate mixture of 42.5 g. II and 1.3 g. of the Na salt of II with 22.8 g. CH2:CHCN on a steam bath 30 min. with shaking, addition of 1 cc. HOAc in 110 cc. boiling C6H6, and chilling the hot filtrate gave 52.5 g. 6-methyl-R-1-propionitrile (XXIII), m. 109-10° (from EtAc). Slightly lower yields resulted with 50% aqueous KOH, powdered NaOH, and Triton B (with dioxane) as catalysts. Pyrolysis of XXIII gave CH2:CHCN and II easily. XXIII (18.4 g.), 92 cc. H2O, and 6 cc. H2SO4 refluxed 3 h. and chilled gave 18.9 g. 6-methyl-R-1-propionic acid (XXIV), m. 165-6° (from H2O, then Me2CO). Esters of XXIV could not be prepared by alcoholysis of XXIII, or from II Na salt and BrCH2CH2CO2Et, XXIV and EtOH-HCl, Ag salt of XXIV and MeI or EtI, II and CH2: CHCO2Et, or XXIV and CH2N2. The oily products always decomposed into acrylic ester and II when distilled, and treatment with K, KOEt, and NaH to remove ROH and give a pyridopicoline ring failed. Addition of 10.9 g. II, then 18 g. BrCH2CO2Et, to 2.3 g. Na in 50 cc. EtOH and 20 cc. C6H2, 2 h.' refluxing, concentration in vacuo to a small volume, addition of 100 cc. H2O, and CHCl3 extraction of the steam distillate gave 1 g. 2-(carbethoxymethoxy)-6-methylpyridine, b15 132°, nD20 1.4909. Addition of 2 g. K2CO3 to the steam-distillation residue and continuous CHCl3 extraction gave 13.7 g. Et 6-methyl-R-1-acetate (XXIVa), m. 81-2° [from C6H6-ligroin (b. 30-60°), then Me2CO-ligroin]. Saponification of 1.24 g. with 7.4 cc. of boiling 35% aqueous KOH 30 min. and addition of 10 cc. H2O and 5.7 cc. HCl gave 0.68 g. 6-methyl-R-1-acetic acid (XXV), m. 229° (effervescence) (from EtOH). XXV was also made in 21% yield from 2.18 g. II, 4.62 g. 50% aqueous KOH, and 1.98 g. ClCH2CO2H boiled 2 min. and 2 cc. H2O added, with 3 min.'s boiling, cooling, solution in 7 cc. hot H2O, addition of 1.8 cc. concentrated HCl, and chilling. Addition at 0° of 2.84 g. Et2C2O4 to 0.76 g. K in 4.3 cc. EtOH and 9 cc. Et2O, then after 10 min. 3.48 g. XXIVa, then C6H6 15 and Et2O 26 cc., and maintenance under a N atmospheric at room temperature 19 h. gave 2.42 g. red K salt; treatment with 0.5 cc. concentrated H2SO4 and 20 g. ice and crystallization from EtOH gave 1.61 g. Et 1-(carbethoxymethyl)-R-6-pyruvate, m. 137-8°. II (2.18 g.), 7.12 g. N-bromosuccinimide, and 0.25 g. Bz2O2 in 60 cc. boiling CCl4 30 min., hot filtration, concentration to dryness, and crystallization from 95% EtOH gave 1.2 g. 3,5-dibromo-6-methyl-R, m. and mixed m.p. 254-5°. Dropwise addition of 18.7 g. Br during 15 min. at 0° to 10.8 g. I in 47 g. 20% H2SO4, shaking 15 min. at room temperature, and addition to the colorless solution at 0° of 80 g. cold aqueous 20% NaOH gave 9.3 g. 2-amino-5-bromo-6-methylpyridine (XXVI), m. 83-4° [from ligroin (b. 90-110°)]. Addition of 32 g. Br below 35° to 10.8 g. I in 47 g. 20% H2SO4, 2 h.

on the steam bath, and chilling 16 h. gave 24.6 g. crude sulfate. Addition in small portions to 50 g. 10% aqueous NaOH at 0° and crystallization from 95% EtOH gave 17.15 g. 2-amino-3,5-dibromo-6-methylpyridine (XXVII), m. 144°. Diazotization of 8.4 g. XXVI in 20% H2SO4, dilution with H2O, 5 min. on the steam bath, addition of 9 g. K2CO3 in 15 g. H2O, and boiling, then chilling and crystallization from 95% EtOH and C6H6, gave 6.9 g. 5-bromo-6-methyl-R, m. 204°. Similarly prepared in 97% yield from XXVII, 3,5-dibromo-6-methyl-R m. 254-5° (from C6H6, then 95% EtOH) [cf. m.p. of 238-9° by Errera (Ber. 33, 2969(1900))].

L7 ANSWER 10 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1948:21270 CAPLUS
DOCUMENT NUMBER: 42:21270
ORIGINAL REFERENCE NO.: 42:4529b-i
TITLE: β-Propiolactone. V. Reaction with alcohols
AUTHOR(S): Gresham, T. L.; Jansen, J. E.; Shaver, F. W.; Gregory, J. T.; Beears, W. L.
CORPORATE SOURCE: B. F. Goodrich Research Center, Brecksville, O.
SOURCE: Journal of the American Chemical Society (1948), 70, 1004-6
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 42:21270
GI For diagram(s), see printed CA Issue.
AB O.CH2.CH2.CO (I) (1 mole), added dropwise to 2 g. Na in 6 moles of the alc. (temperature maintained at 0°), gives the following HOCH2CH2CO2R (yield of Me ester at 25° 76%, of Et ester 69% with 4 g. Me3(PhCH2)NOH): Yield, B.P.; R, %, °C., mm., nD20, d420; Me, 85.1, 71, 13, 1.4225, 1.1153; Et, 80.1, 75, 8, 1.4222, 1.0545; Pr, 65.5, 98, 19, 1.4251, 1.0217; Bu, 77.2, 114, 20, 1.4284, 0.9989; C8H17, 64.5, 104, 4, 1.4392, 0. 9484. The oily residue from the reaction with MeOH is Me β-(β-hydroxypropionoxy) propionate, b0.3 85-6°, nD20 1.4429, d420 1.1902. With secondary alcs., it is more difficult to avoid the polymerization of I, probably because of the slower rate of the primary reaction. The noncatalyzed reaction of I with alcs. is extremely slow and ROCH2CH2CO2H (II) and polymers are the only products. Some esterification of the alkoxy acids occurs, especially with the lower alcs. at higher temps. With secondary and tertiary alcs., these noncatalyzed reactions are still slower, more of I polymerizes, and no esters of the alkoxy acids are isolated. The acid-catalyzed reaction of I with alcs. is extremely complex. II and their esters, esters (III) of HOCH2CH2CO2H, and polyester acids (IV) with terminal alkoxy groups are formed. The composition of the mixture obtained is dependent on the reaction conditions employed, the most important factors of which are the acid catalyst concentration, the temperature, time, and molar excess of alc. Numerous expts. are given (H2SO4 as catalyst) to show the effect of these factors. The quantity of III formed by the secondary reaction increases with time with a corresponding decrease of IV, and none of it formed in incomplete reactions. Polymerization, alcoholysis, and esterification are favored with increasing catalyst concentration and temperature However, with high acid concentration only insol. polymers of higher mol. weight result. Decrease in the excess alc. favors the polymerization. The following consts. are reported:;ROCH2CH2CO2H; B.P.; R, °C, mm., nD25, d420; Me, 102, 13,

1.4160, 1.0982; Et, 108, 10, 1.4178, 1.0450; Pr, 76, 1, 1.4204, 1.0043; iso-Pr, 70, 1, 1.4222, 1.0032; Bu, 72, 0.1, 1.4240, 0.9876; ROCH2CH2CO2R; Me, 63, 40, 1.3993, 1.0052; Et, 60, 13, 1.4041, 0.9461; Pr, 87, 13, 1.4139, O.9369; iso-Pr, 67, 13, 1.4059, 0,9150; Bu, 97, 6, 1.4190, 0.9109. The reaction with MeOH gives Me β-(β-methoxypropionoxy) propionate, bl.5 86°, nD25 1.4260.

L7 ANSWER 11 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1943:37471 CAPLUS
DOCUMENT NUMBER: 37:37471
ORIGINAL REFERENCE NO.: 37:5968d-i,5969a-f
TITLE: An indole synthesis from a m-carboxyphenylhydrazone
AUTHOR(S): Koelsch, C. F.
SOURCE: Journal of Organic Chemistry (1943), 8, 295-9
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
GI For diagram(s), see printed CA Issue.
AB The conversion of lysergic acid (I) into isolyzergic acid may be due to a shift of the double bond from the 2,3- into the 3,4-position involving the rings A, B, and C. An attempt is made to synthesize 1,3-dihydrobenz[cd]indole containing the A, B, C ring system, by the Fischer indole synthesis. m-Aminobenzoic acid (17.3 g.), in 10 cc. concentrated HCl and ice, is diazotized with 7 g. NaNO2. When the solution is clear, 20 g. AcONa.3H2O and 15.6 g. Et cyclopentanone-2-carboxylate is added, giving 2-carbethoxy-2-(m-carboxyphenylazo)cyclopentanone (II) as yellow needles which sinter at 105° and m. 118-20° (decomposition). II, when boiled with 7% Na2CO3 for 2 min. and acidified, gives 70% of the hydrazone m-HO2CC6H4NHN:C(CO2Et) CH2CH2CH2CO2H (III) as orange-brown crystals, m. 165-7°, which when boiled with absolute EtOH and H2SO4 gives the m-carbethoxyphenylhydrazone of di-Et α-ketoadipate, m. 125-7°. When boiled with 10% NaOH III gives the m-carboxyphenylhydrazone of α-ketoadipic acid, m. 215-18° (decomposition). When 165 g. III in 250 cc. absolute EtOH and 75 cc. concentrated H2SO4 is boiled for 2 h. and, after addition of another 75 cc. H2SO4, for an addnl. 3 h., 2,6-dicarbethoxy-3-(2-carbethoxyethyl) indole (IV) and (NH4)2SO4 crystallize on cooling. The latter is removed by washing with H2O. The alc. mother liquor is diluted with H2O and extracted with ether. The ether extract, after being washed with Na2CO3 and concentrated, gives a 2nd crop of IV.
The ether mother liquor is evaporated to dryness and the residue redissolved in ether. Addition of petr. ether causes the separation of crude 2,4-dicarbethoxy-3-(2-carbethoxyethyl)indole (V). The acids obtained on acidification of the Na2CO3 extract, when boiled with EtOH in H2SO4 for 3 h., give some more V. IV (40-g. yield), recrystd. from EtOH, crystallizes with 0.5 mol. EtOH and m. 113°. V (58-g. yield) m. 105-6° after several crystns. from ether-ligroin. Oxidation of 5 g. IV in 25 cc. AcOH by slow addition of 4 g. CrO3 in 13 cc. AcOH and 2 cc. H2O at 25-30°, gives 4.6 g. Et β-(4-carbethoxy-2-ethoxalylaminobenzoyl)propionate (VI), m. 97-9°. Oxidation of V in the same way gives Et β-(6-carbethoxy-2-ethoxalylaminobenzoyl)propionate (VII), m. 84-6°. When VI is boiled with alkali, a yellow product, m. above 225°, probably 2,7-dicarboxy-4-hydroxy-3-quinolineacetic acid, is obtained. Alcoholysis of VI by boiling it for 3 h. with EtOH containing H2SO4 gives Et β-(2-amino-4-carbethoxybenzoyl) propionate (VIII),

bright yellow plates, m. 87-8°; Bz derivative, m. 86-8°, when boiled with aqueous NaOH gives a white crystalline acid, probably a quinoline derivative, which sinters and darkens at 210°. VII and EtOH containing H2SO4 give Et β-(6-carbethoxy-2-aminobenzoyl) propionate (IX) as a colorless basic oil. Diazotization of VIII and IX in H2O or alc. gives only oily products. Diazotization of 4.5 g. VI in 25 cc. EtOH containing 2 cc. H2SO4 at 0° with BuONO gives the cinnoline (X), m. 168-71°. VII, under the same conditions, gives an oil which when boiled with 10% KOH gives β-(2-ethoxy-6-carboxybenzoyl)propionic acid, m. 166-8°. When VIII is boiled for 0.5 h. with 10% NaOH and the mixture acidified with H2SO4 to pH 3, β-(2-amino-4-carboxybenzoyl)propionic acid, bright yellow needles which do not m. 250°, is obtained. When immersed in a bath above 215°, it partially m., then resolidifies and becomes much ligher in color. IX under the same conditions gives β-(2-amino-6-carboxybenzoyl)propionic acid, flat tan needles, sinters 168° and m. 180° with gas evolution. From the mother liquor, 4-amino-1,3-diketo-2-hydrindeneacetic acid, sinters 192° and m. 202° with darkening, is obtained. It gives a deep red solution with Na2CO3 and a pale yellow solution with HCl.

L7 ANSWER 12 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1941:26771 CAPLUS
DOCUMENT NUMBER: 35:26771
ORIGINAL REFERENCE NO.: 35:4234g-i,4235a-g
TITLE: The composition and source of the "esters" in distilled glycerol
AUTHOR(S): Tyutyunnikov, B.
SOURCE: Seifensieder-Zeitung (1941), 68, 57,70-1,82,92,103-4
CODEN: SSZTAW; ISSN: 0371-3296
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
AB Glycerol from the first condenser of a Van Ruymbeke still may contain Ca salts of higher fat acids, carried over by entrainment. Glycerol from the 2nd condenser may contain higher fat acid mono esters of glycerol which have distd: Both portions, especially the 2nd, may contain esters of caproic and higher acids. Under the usual analytical conditions, heating on the water bath with excess alkali for 15 min. is insufficient to saponify all of the esters. This may be due to the presence of lactones, etc., occurring in varying amts. The esters found in distilled glycerol are formed in the vapor state. Fat acids are set free from soaps by alcoholysis during distillation and are carried over in the steam if excess alkali is absent. A high content of salts of sulfonaphthenic acids may be present in saponification glycerol if the "Kontakt reagent" was made from kerosene. These acids during distillation of glycerol behave similarly to fat acids. Expts. showed that HOAc is distilled with glycerol from a glycerol solution of NaOAc. Formic acid under similar conditions appears in the distillate to a lesser extent. The weight of free alkali in the residue from distillation of sapon glycerol is much less than would be calculated from the weight and composition of the charge. Corresponding proportions of acids were formed during distillation Part of these came from the sulfonaphthalene salts. Aldehydes and acetates were practically absent from the distilled glycerol. Formic acid took an important part in the reactions. The aqueous distillate, when it contained free acids and

lactones, gave a pos. test for lactic acid. When the ether number was 0 or very small, the test for lactic acid was neg. Formic and lactic acids are not present in fats and are formed in industrial distillation of glycerol. At 280°, with excess of caustic alkali, glycerol yields propylene glycol, CH3OH, HCOOH, (COOH)2 and C2H5COOH. In absence of excess alkali, lactic acid is formed. With excess alkali, the lactic acid decomposes to CO2, HCOOH, CH3COOH and C2H5COOH. In absence of a large excess of alkali, lactic salts change to those of dilactylic acid. Similar reactions must occur during prolonged heating at 180° in the Van Ruymbeke still. The presence of formic and acetic acids in glycerol distillation residues can be explained thus: CH2:CHCHO + H2O → CH2OHCH2CHO; CH2OHCH2CHO + H2O → H2C(OH)2 + CH3CHO; H2C(OH)2 → HCHO + H2O; 2HCHO + H2O → HCOOH + CH3OH; CH3CHO + HCHO + H2O → CH3COOH + CH3OH. The last equation occurs only to a very slight extent. Similar reactions may occur during hydrogenation in autoclaves. Acetaldehyde was found in some "sweet waters." No MeOH was found probably because of the difficulty of separation The reactions suggest the method of formation of propylene glycol during distillation The formation of lactates, dilactylates and formates also is explainable. They may be carried over by entrainment. Liquid recovered from the entrainment separators had sp. gr. 1.355 and ash content 5.5%. T. concludes: both lower and higher acids participate in ester formation. Salts of higher and lower fat acids, of lactic acid and lactides, when present in distilled glycerol are due to entrainment, which is also responsible for poor color. Formic acid is formed by reaction of acrolein and water vapor; also by reaction of glycerol and caustic alkali. The formation of lactic acid is due to the same reaction. Fat acids, from acetic upward, appearing in glycerol vapors are to be attributed to alcoholysis of their salts. The decrease in ester content of distilled glycerol by the introduction of excess alkali into the crude glycerol is to be attributed to the lessening of alcoholysis of soaps and the condensation of aldehydes into nonvolatile compds. The consumption of caustic alkali during distillation is to be explained by the reaction of the alkali with glycerol or with foreign substances present.

L7 ANSWER 13 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1937:44783 CAPLUS
DOCUMENT NUMBER: 31:44783
ORIGINAL REFERENCE NO.: 31:6244d-i,6245a-b
TITLE: Strychnine and brucine. XXXVI. Preliminary synthetical experiments
AUTHOR(S): Openshaw, H. T.; Robinson, Robert
SOURCE: Journal of the Chemical Society (1937) 941-6
CODEN: JCSOA9; ISSN: 0368-1769
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
GI For diagram(s), see printed CA Issue.
AB The object of the present expts. is to approach the strychnine skeleton as closely as may be in the hope that some degradation product may be synthesized. The preparation of Et 2-carbethoxycyclohexanone-2-β-propionate (IA) in 80% yield is described and also its hydrolysis with concentrated HCl to give 90% of cyclohexanone-2-β-propionic acid. The oily phenylhydrazone with boiling 20% H2SO4 gives the lactam of tetrahydrocarbazole-1-β-propionic acid (I), plates with a bluish tinge, m. 126° and tetrahydrocarbazolenine-11-β-propionic acid (II), m. 226°, the latter being soluble in dilute acids or alkalies. I was not reduced with H2 and Pt, Sn and dilute EtOH-HCl or with Na and EtOH

or iso-AmOH; electrolytic reduction at a Pb cathode in AcOH-H2SO4 gives 1,9-trimethylenehexahydrocarbazole (III), m. 81-2°; addition of a trace of FeCl3 to a solution in 5% HCl gives an intense red color. Dehydrogenation of III by Hg(OAc)2 in AcOH or by heating with Pd-C gives 1,9-trimethylene-1,2,3,4-tetrahydrocarbazole, m. 87-8°; boiling Ehrlich's reagent gives a bluish green color, which fades to yellow on cooling. Reduction and acetylation of II yield N-acetylhexahydrocarbazole-11-β-propionic acid, m. 202°; in 60% H2SO4 it gives an intense reddish purple color with K2Cr2O7, which fades rapidly through red to brownish yellow. Refluxing IA and EtOH-EtONa for 8 h. gives Et 6-carbethoxycyclohexanone-2-β- propionate, b11 189-90° (70% yield); FeCl3 gives a deep violet color; this reaction is obviously alcoholysis and ring closure in a new position. With Na and ClCH2CH2CO2Et in C6H6 there results 75% of Et 6-carbethoxycyclohexanone-2,6-β,β'-dipropionate (IV), b0.2 182-3°; condensation in EtOH gives a poor yield of IV and a considerable quantity of Et heptane-1,3,7-tricarboxylate, b0.15 147-8°; Na in C6H6 with a trace of EtOH and ClCH2CH2CO2Et give 80% of IV. Hydrolysis of IV with concentrated HCl gives 98% of cyclohexanone-2,6-β,β'-dipropionic acid, m. 145°; Et ester, m. 60-1°; the orange, oily phenylhydrazone with EtOH-HCl, followed by reduction with Sn, yields the lactam. of hexahydrocarbazole-1,11-β,β'-dipropionic acid (V), m. 269-70°; K2Cr2O7 in 60% H2SO4 gives a transient purple color, fading through rose-red to yellow.

L7 ANSWER 14 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:	1906:152300 CAPLUS
DOCUMENT NUMBER:	0:152300
TITLE:	On the Preparation of Pure Alkyl Malonic Ester. [machine translation]
AUTHOR(S):	Michael, A.
CORPORATE SOURCE:	TUFTs Coll. Chem. Lab.
SOURCE:	Journal fuer Praktische Chemie (Leipzig) (1905), 72, 537-54 From: Chem. Zentr., 1906, I, 745-747 CODEN: JPCEAO
DOCUMENT TYPE:	Journal
LANGUAGE:	Unavailable

AB [Machine Translation of Descriptors]. (See CONRAD, LIEBIG's Ann. vo. 204, pg. 134; Z. f. Phys. Ch. vo. 7, pg. 285; C. vo. 91, I. pg. 910; SCHEY, Rec. trav. Chim. Pays-Bas vo. 16, pg. 357; C. vo. 98, I. pg. 28; MICHAEL, Ber. German Chemistry Society vo. 38, pgs. 2091, 3217; C. vo. 1905, II. pgs. 396, 1665) the CONRAD method, effect of ethyl iodide on sodium malonic ester to alcoholic solution, supplies with the ethyl malonic ester contaminated by diethyl malonic ester. The proof of this non-uniformity is based on it that malonic ester of aqueous potash each concentration becomes fast into the potassium ethyl salt, the mono-alkyl malonic ester by diluted alkali analogous decomposing, against 25% Alkali however are rather stable, the dialkyl malonic ester of concentrated or also very much diluted alkali was only slowly saponified. With the help of this method, which is applicable both for the separation of these esters, and for the proof of their purity, in the CONRAD mono-ethyl malonic ester about 15% diethyl esters were proven, and due to the inadequacy a number on such compounds requires the parliamentary group method for the purification of such compounds based investigations of the repetition. Thus the formation goes from Butane-α, β, β-tricarbon ester from sodium ethyl malonic ester and chloroethyl acetate many more smoothly indicated before

itself, than of BISCHOFF and V. KUHLBERG (Ber. German Chemistry Society vo. 23, pg. 638; C. vo. 90, I. pg. 752). For the easy production of more uniform Alkyl malonic ester, heating a mixture of potash powdered by sodium malonic ester and alcohol with a Alkyl halide and registering into a mixture are suitable malonic ester and an alkyl iodide; latter method is applicable also to alkylated acetoacetic acid. The increase of the ease of the saponifiability from dialkyl to Monoalkylmalonic ester and to malonic ester (methyl derivatives are more easily more saponifiable than ethyl and propyl derivatives) continues to stand in contradiction from E. FISCHER (Ber. German Chemistry Society vo. 31, pg. 3266; C. vo. 99, I. pg. 339; see also E. FISCHER and VAN'T HOFF, Ber. German Chemistry Society vo. 31, pg. 3277) set up statement, according to which the ability exerts a retarding influence on the saponifiability for salt formation of esters; with the alkaline. Hydrolysis attacks that alkali in the molecule, where most free negative energy is present, that is, here CO to the ester. If larger neutralization of the atoms of the carbonyl is caused (therefore conversion of free energy into bound) by a change of constitution, for example by introduction of the sodium to acetoacetic esters, then this means a relative protecting of the carbonyl against addition of the alkali, i.e. an aggravation of the hydrolysis. With the Natroacetoacetic ester also decomposes into aqueous solution after GOLDSCHMIDT and OSLAN (Ber. German Chemistry Society vo. 32, pg. 3392; C. vo. 1900, I. pgs. 171, 1070) only the small part of the ester of alkali, which is released into aqueous solution of the salt. Malonic ester neutralized Na far less than acetoacetic esters; here so much free positive energy comes to the metal that it under effect of water alcoholysis causes immediately, as the free energy of the metal changes by entrance into the carboxyl group well into bound energy and heat. The metal derivatives of the uric acid are well neutralized; those of the Tetramethyl uric acid, which are in fewer neutralized, are more easily decomposable by the relatively larger content of the CO group at free negative energy. The ease of the addition at the CO group indirectly atoms and their spatial position in the molecule affect strong; to it the slowing down of the hydrolysis of the dimethyl to the diethyl malonic ester and amide formation of the not substituted is to be led back over the monalkylated to dialkylated malonic ester; of E. FISCHER and DILTHEY (Ber. German Chemistry Society vo. 35, pg. 844; C. vo. 1902, I. pg. 745) set up theory does not explain these facts. Experimental part; Malonic acid; 1 part Potassium salt in 160 parts water does not give a precipitate with CaCl2. Diethyl ester. All over cyanogen acetic acid was prepared or available malonic ester contains N. for the removal of cyanogen ethyl acetate vibrates one raw malonic ester twice with diluted NH3; its potassium compound develops from the ester and 50%igem potash, existed temporarily with presence of water, is crystalline and turns with water rapidly into alcohol and Potassium ethylmalonate. This develops also from malonic ester and aqueous KOH, also for such from 25%; perhaps the hydrolysis, which is all the more rapidly effected, the more diluted the potash solution, most rapidly with 1% igem, goes over above potassium compounds. Mono-ethyl malonic acid diethyl ester; for the preparation, one adds to 300 g dry ether and 14.4 g Na (without crushing) 100 g of malonic ester, agitates well, heated to the disappearance of the sodium on the water bath, adds 100 g ethyl iodide, heated, after the reaction diminished up to the neutrality of the mixture on the water bath, initially removed with water, then with diluted Na2CO3-solution and fractional; to the purification one vibrates 75 g briefly with 40 g 25%igem potash, boils insoluble. Oil (67 g) with 25 g KOH in 100 ccm water, registers then unresolved in 25g KOH in 30 g H2O, removes the diethyl ester by ether

removal, boils with further, 20%igem alkali (so that the quantity of the alkali amounts to 70 g) to about 2 hours, diluted to 1 l, neutralized with HCl and settles with CaCl2; the salt dried in the vacuum supplies nearly pure ester with the esterification of 46 g; ethyl iodide and 3.6 g powdered potash develop also from 10 g of malonic ester, for 10 g; Kp748, 211° (corrected) under small decomposition; Kp10, 92°; D200, 1.004. Mono methyl malonic acid diethyl ester; from sodium malonic ester in ether was produced, and methyl iodide; one adds KOH powdered by 20 g of malonic ester and 18 g methyl iodide gradually 8 g to a mixture, heated to the accomplished conversion on the water bath, intersperses water too, vibrated well and dries the oil over CaCl2, - Kp765, 198.5 to 199° (corrected), by alkali one decomposes. Monopropylmalonic acid diethyl ester, Kp771, 225.5 to 226° (corrected), D250, 0.9897. Are event from the Monoalkylmalonic ester prepared to dialkyl malonic ester like these from malonic ester and the effect of Alkyl halide and potash was repeated. Dimethylmalonic acid diethyl ester, Kp765, 196 to 196.5°, becomes slow by KOH of 25%, of 50% rapidly saponified. Diethyl malonic acid diethyl ester, with boiling point of 228.5-229.5° (corrected). For the proof in presence of mono ethyl and malonic ester with 50%igem, then with 25%igem KOH one vibrates briefly; with the diluting with water it separates then in the form of oil droplets: the presence of mono ethyl malonic ester in the diethyl malonic ester indicated by a white precipitate also with 20° saturated KOH solution. Dipropylmalonic acid diethyl ester, with boiling point of 248 to 249°. Ethylacetoacetic acid ethyl ester, from acetoacetic esters C2H5I and powdered KOH. Diethylacetoacetic acid ethyl ester, from ethylacetoacetic acid ethyl ester, ethyl iodide and powdered KOH.

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     (FILE 'HOME' ENTERED AT 09:59:01 ON 18 SEP 2008)

     FILE 'CAPLUS' ENTERED AT 09:59:39 ON 18 SEP 2008
L1          2441 S (?ESTERIFICATION) (L) ((METHYL (A) ACETATE) OR (ETHYL (A) ACE
L2           177 S L1 (L) (FAT# OR OIL#)
L3            27 S L2 AND (LIPASE OR ENZYME)
L4            14 S L3 AND FUEL
L5             3 S L1 (L) (FATTY (A) ACID (A) ALKYL (A) ESTER)
L6           116 S ALCOHOLYSIS (L) ((METHYL (A) ACETATE) OR (ETHYL (A) ACETATE)
L7            14 S L6 (L) (FAT# OR OIL#)
L8             0 S L7 (L) (FATTY (A) ACID (A) ALKYL (A) ESTER)
L9             0 S L7 AND FUEL
L10            0 S L7 AND (FATTY (A) ACID (A) METHYL (A) ESTER)

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ALL L# QUERIES AND ANSWER SETS ARE DELETED AT LOGOFF
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STN INTERNATIONAL LOGOFF AT 10:14:57 ON 18 SEP 2008
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